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Catalyst Evaluation for Denitrogenation of Petroleum Residual and Coal Liquids

Hydrocarbon Research, Inc, Lawrenceville, NJ

Prepared for

Industrial Environmental Research Lab, Research Triangle Park, NC

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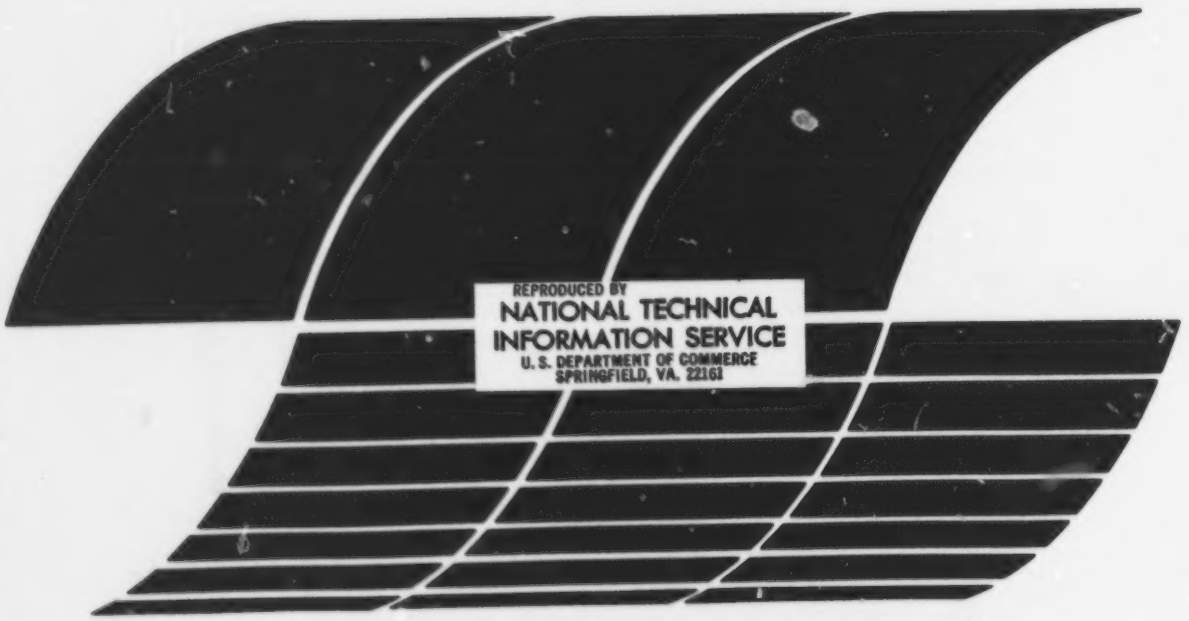

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16. ABSTRACT The report covers the final phase of a study of catalysts for demetallization of heavy residual oils and for denitrogenation. Objectives were to evaluate some commercial catalysts for denitrogenation activity in petroleum residua and coal liquids, and then to develop an improved catalyst for denitrogenation of heavy coal liquids. Under one task, two commercial catalysts failed to reduce nitrogen content of a petroleum vacuum resid from 0.67% to the 0.3% target. The observed catalyst deactivation rate is similar to that of catalysts with similar pore structures which are being used for hydrodesulfurization of petroleum resid. Under another task, attempts to denitrogenate heavy coal-derived liquids with commercial Co-Mo catalysts pointed to the need for improved catalysts. In the task to improve catalysts, Ni-Mo was identified as a better active metal pair than Co-Mo or Ni-W for denitrogenation of coal liquids. Commercial preparation techniques and lower carbon deposition also increased denitrogenation activity. On the basis of catalyst weight, a bimodal pore distribution with some macropores showed better denitrogenation activity than that with micropores only. Efforts to find the optimum pore distribution were hampered by lack of technology to enlarge macropores. One experimental catalyst was tried. Denitrogenation activity did not decrease despite a low surface area.

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Coal	Coal Liquefaction	21D
Liquefaction	Denitrogenation	07D
Nitrogen	Demetallization	07B
Catalysts		
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Catalyst Evaluation for Denitrogenation of Petroleum Residua and Coal Liquids

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ABSTRACT

This report describes the results of a study of catalysts for denitrogenation of petroleum residua and coal liquids. The objectives were to evaluate some existing commercial catalysts for denitrogenation activity in petroleum residua and coal liquids and then to develop an improved catalyst for denitrogenation of heavy coal liquids. Under task two, commercial catalysts failed to reduce nitrogen content of a petroleum vacuum resid from 0.67 percent to the target of 0.3 percent. The observed catalyst deactivation rate is similar to that of catalysts with similar pore structures which are being used for hydrodesulfurization of petroleum resid. Under another task, attempts to denitrogenate heavy, coal-derived liquids with commercial Co-Mo catalysts pointed to the need for improved catalysts. In the task to improve catalysts, Ni-Mo was identified as a better active metal pair than Co-Mo or Ni-W for denitrogenation of coal liquids. Commercial preparation techinques and lower carbon deposition also increased denitrogenation activity. On the basis of catalyst weight, a bimodal pore distribution with some macropores showed better denitrogenation activity than that with micropores only. The optimum pore distribution was sought, despite lack of technology to enlarge macropores. Unusual catalyst preparation techniques were tried but only one catalyst was prepared and evaluated for the effects of more and larger macropores. It has a low surface area and its denitrogenation acitivity relative to the base catalyst did not decrease. If this were a general result for catalysts with more and larger macropores, less metals would be needed to cover the support and a lower cost catalyst could be developed.

Hydrocarbon Research, Inc., a subsidiary of Dynalectron Corporation, did this work as Phase V of Contract 68-02-0293 with the U.S. Environmental Protection Agency. The period of performance of the entire contract was December 1972 through February 1978 and included the study of demetallization of heavy residual oils. Phase V work was done from September 1975 through February 1978.

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CONVERSION FACTORS FOR U. S. ENGINEERING UNITS TO SI UNITS

Given U. S. Unit	Multiply By	Obtain SI Unit
inch	0.0254	m (meter)
mm	1×10^{-3}	m
cm	1×10^{-2}	m
Å (angstrom)	1×10^{-0}	m
bbl (barrel)	0.1590	m^3 (meter ^{3})
gal (gallon)	0.00379	m^3
cu.ft. (ft^3)	0.02832	m^3
cc (cm^3)	1×10^{-6}	m^3
lb. (pound)	0.00454	kg (kilogram)
gm (gram)	1×10^{-3}	kg
psi (lb/in^2)	6.895	kpa (kilo Pascal)
cp (centipoise)	1×10^{-3}	Pa·S (Pascal·Second)

Temperature Conversion:

^{o}K (Kelvin) = [^{o}F (Fahrenheit) +459.6] ÷ 1.8

^{o}C (Celsius) = [^{o}F (Fahrenheit) - 32] ÷ 1.8

SECTION 1

SUMMARY

This report covers work done under Phase V of Contract No. 68-02-0293 funded by the Environmental Protection Agency. The objectives of this final phase were to evaluate a number of commercial catalysts for denitrogenation of petroleum residua and coal liquids, and to develop an improved catalyst for denitrogenation of heavy coal liquids. Three main tasks comprise the work done in this phase.

Under Task 1, two commercial catalysts were evaluated for the denitrogenation of a petroleum vacuum resid. Under mild operating conditions: 780°F*, 2000 psig and 0.85 liquid hourly space velocity (LHSV), both catalysts failed to reduce the nitrogen content of the feed from 0.67 to 0.3%, which is the target set by EPA for this project. American Cyanamid Ni-Mo trilobe catalyst HDS 9A possesses only micropores. It showed higher level of denitrogenation, but a much faster rate of deactivation than the American Cyanamid Co-Mo catalyst HDS 2A possessing both macropores and micropores. This type of catalyst deactivation exists among catalysts with these pore structures upon hydrodesulfurizing of petroleum resid.

Task 2 evaluated two commercial catalysts to remove nitrogen from a gas oil product and a fuel oil product from the H-Coal® Process. Under mild operating conditions, a commercial Co-Mo catalyst, Harshaw HT-400, reduced effectively the nitrogen content of the coal-derived gas oil from 0.45 to 0.1% which is sufficiently low for utilization as turbine fuel. The H-Coal fuel oil product contained 0.8% nitrogen and 35% resid. The catalyst used was American Cyanamid HDS 2A, which has been used for hydroprocessing of petroleum resid and also for coal liquids. Severe operating conditions were set at 810°F, 2800 psig, and 0.5 LHSV, attempting to meet the target of 0.3% nitrogen. The nitrogen content was reduced from 0.84 to 0.28% initially, but at the end of 3-day operation, the nitrogen content of the liquid product rose to 0.39%. The data confirmed the need for improved catalysts for denitrogenation of heavy coal-derived boiler fuel.

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*EPA policy is to use SI units. Non-metric units are used in the text of this report to increase its utility to the U. S. engineering community. Conversion factors to SI units are given on page vi.

Task 3, consisting of three subtasks, was undertaken to develop a denitrogenation catalyst better than the base Co-Mo catalyst, American Cyanamid HDS 2A, for use on heavy coal liquids produced from the Solvent Refining Coal Process. A 60/40 blend of recycle solvent/SRC product was prepared to yield a feedstock pumpable at 150°F. Nearly 35 percent by weight of this blend consists of residua with boiling points above 975°F. The total liquid contains about 88 percent carbon, 7 percent hydrogen, 1 percent nitrogen, 0.6 percent sulfur and 3 percent oxygen.

Subtask 3A evaluated the denitrogenation capability of three pairs of active metals: Co-Mo, Ni-Mo, and Ni-W. Ni-Mo had higher denitrogenation activity than either Co-Mo or Ni-W. The following factors affecting catalyst activity were studied: method of catalyst preparation, operating temperature upon Co-Mo, Ni-Mo and Ni-W catalysts, operating pressure upon Co-Mo, Ni-Mo and Ni-W catalysts, and feedstock upon Ni-Mo catalyst. Four catalysts prepared by using the commercial technique exhibited higher activity than those prepared by an impregnation method. Operating parameters giving lower carbon deposition on the catalysts resulted in higher denitrogenation activity. These are: operating temperature lowered from 850 to 810°F, operating pressure raised from 2000 to 2800 psig, and feedstock containing no 975°F+ resid.

Subtask 3B evaluated the significance of bimodal pore size distribution in the Ni-Mo catalyst. A catalyst with bimodal pore size distribution and high pore volume exhibited the same activity during the 3-day test as the corresponding catalyst with a single-modal pore size distribution. Since the weight of catalyst charged to the reactor was 30% higher for the single-modal than the bimodal catalysts, the data indicated that incorporating macropores into the catalyst extrudates improves denitrogenation activity per unit of catalyst weight.

The objective of Subtask 3C was to improve the catalyst activity through optimization of the bimodal pore size distribution of the catalyst. Armak was subcontracted to prepare four Ni-Mo catalysts with larger macropores and/or larger micropores while maintaining the same total pore volume as the base catalyst. The technology is available for enlarging the micropores. Armak undertook extrusion research to develop a technique for increasing and enlarging the macropores, but they had limited success.

Data for the Armak catalysts were directly compared to data from the base catalyst. A catalyst with lower macropore and micropore volume than in the base catalyst showed a pronounced decrease in denitrogenation activity on a catalyst weight basis. Lower macropore volume alone also caused a decrease. The effect of larger micropores was masked by smaller micropore volume or inferior preparation technique compared to the base catalyst.

The data derived from the evaluation of the only Armak catalyst with larger and more macropores than the base catalyst did not show any significant increase in denitrogenation activity. However, the Mo-containing

extrudates were calcined at high temperature to reduce total pore volume to that of the base catalyst. This unusual method of preparation might have an adverse effect on the catalyst and prevents a conclusion from being reached about the effect of increasing and enlarging the macropores. However, this catalyst did have a low surface area which presumably needs less metals for covering the catalyst support. If denitrogenation activity is not decreased, a low cost catalyst could result from seeking more and larger macropores.

The effect of space velocity was investigated for the catalyst with larger and more macropores by conducting two 15-days runs at 0.5 and 1.0 LHSV. At 0.7 bbl/lb catalyst age, a run at 0.5 LHSV showed a steep deactivation whereas a run at 1.0 LHSV did not. At 0.8 bbl/lb catalyst age, the former showed lower denitrogenation activity than the latter. It is likely that operating at lower space velocity gave deeper 975^{0}F+ resid conversion initially. This resulted in higher carbon deposition on the catalyst, which led to steeper catalyst deactivation.

SECTION 2

CONCLUSIONS

Experimental results allow certain conclusions to be made as follows:

- The denitrogenation activity of a catalyst decreased markedly with increasing specific gravity or increasing boiling range of the feedstock. Denitrogenation of petroleum resid was as difficult as that of coal-derived resid. Carbon deposition on catalyst from H-Coal or SRC gas oil boiling range feedstock was only about half of the amount from feedstock containing about 35% of 975^{o}F+ material. For denitrogenation of coal derived gas oil, commercial Co-Mo catalyst was capable of reducing the nitrogen content to as low as 0.1%, which is the level suitable for use as turbine fuel.

- Regarding active metals, Ni-Mo has higher denitrogenation activity than either Co-Mo or Ni-W. The Ni-Mo catalyst possesses the unique feature of being more active at 810^{o} than at 850^{o}F.

- Regarding pore size distribution, a Ni-Mo catalyst with bimodal pore size distribution and higher pore volume exhibited the same activity as the corresponding catalyst with single-modal pore size distribution and lower pore volume. In general, Ni-Mo catlayst with much lower surface area did not lose denitrogenation activity. The lowering of surface area resulted from larger and more macropores or larger micropores.

- Evaluation of one Ni-Mo catalyst with significantly more and larger macropores did not lead to any conclusion about the expected beneficial effect. The unusual method used in preparing this catalyst could have had an adverse effect upon its denitrogenation activity.

- Regarding catalyst deactivation, most of the activity loss in 3-day tests was due to carbon deposition on catalysts. Operating parameters resulting in high carbon deposition frequently produced low denitrogenation activity. These parameters included low hydrogen pressure, high temperature to certain levels and feedstock with high boiling temperatures.

- Regarding effect of space velocity, 15-day runs at two space velocities with the catalyst having more and larger macropores disclosed that deeper resid conversion achieved at low space velocity resulted in high carbon deposition on the catalyst, which caused steeper deactivation than operating at high space velocty. At a catalyst age greater than 0.8 bbl/lb, low space velocity operation gave a significantly lower level of denitrogenation than did the high space velocity operation.

SECTION 3

INTRODUCTION

The New Source Performance Standards set by the U.S. Environmental Protection Agency for stationary sources specify a maximum nitrogen oxide fuels, fixation of atmospheric nitrogen during the combustion process is the primary source of this emission. If organic nitrogen is present, roughly one-third of the organic nitrogen content of the fuel can react to form nitrogen oxides (NO_x), the degree of conversion depending on firing methods. At the conversion of one-third of the nitrogen content of fuel oil to NO_x, this contributes 500 ppm of NO_x per percent of nitrogen in fuel oil, over and above that from the fixation mechanism. Some petroleum resids contain close to 1% nitrogen. Most of the coal liquids contain more than 1% nitrogen. Hence processing of high nitrogen-containing petroleum resid and coal liquids may be required to enable them to be used as boiler fuel for stationary power plants. The target set by EPA for this program is a maximum of 0.3% nitrogen in fuel oil.

A program was undertaken to evaluate commercial catalysts for denitrogenation of petroleum resid and coal liquids, and to develop an improved catalyst for denitrogenation of heavy coal liquids.

Under Task 1, two commercial catalysts, American Cyanamid HDS 2A and HDS 9A, were evaluated for denitrogenation of a Gach Saran vacuum resid.

Task 2 investigated the denitrogenation of a gas oil product and a fuel oil product containing 30% resid from the H-Coal Process. A commercial Co-Mo catalyst with only micropores, Harshaw HT-400, was used for the gas oil feed, and a commercial Co-Mo catalyst with both micropores and macropores, American Cyanamid HDS 2A, was used for the fuel oil feed. The gas oil feed was processed at mild operating conditions, mild and severe, to determine the rate of catalyst deactivation.

The task 3 was devoted to developing an improved catalyst for denitrogenation of heavy coal liquids. A blend of 40% SRC product and 60% SRC solvent was used as the feedstock. Task 3 consisted of three subtasks.

Subtask 3A compared the denitrogenation activity of 3 metal pairs: Co-Mo, Ni-Mo, and Ni-W. The current commercial hydrotreating and hydrocracking catalysts contain cobalt-molybdenum, nickel-molybdenum, or nickel-tungsten as the active metal pairs. It is known that in general the hydrotreating (desulfurization with minimum ring saturation) capabilities of these three pairs of active metals are: Co-Mo > Ni-Mo > Ni-W, whereas their hydrocracking

capabilities are in the opposite order: Ni-W > Ni-Mo > Co-Mo.

In view of the stable nature of the nitrogen compounds present in the coal liquids, catalyst possessing somewhat higher hydrocracking capability than current commercial hydrotreating and hydrocracking catalysts might be desirable. Therefore, the denitrogenation capability was compared among the catalysts containing these three metal pairs on a γ-alumina support at the same pore volume level with similar pore size distribution.

The objective of Subtask 3B was to establish the significance of the bimodal pore size distribution of Ni-Mo catalyst.

The objective of Subtask 3C was to improve the catalyst activity through pore size optimization. It has been established in H-Coal operations that the pore size distribution of the Co-Mo catalyst plays an important role in catalyst activity and the rate of deactivation. The presence of sufficient macropores is essential for good performances in terms of coal conversion, resid conversion and desulfurization. The conversion of 975^{o}F+ resid to lower boiling materials seems to be the rate limiting step. The 500^{o}F+ fuel oil fraction produced from the H-Coal processing of Illinois No. 6 coal contains about 70% 975^{o}F+ resid which has a nitrogen content of 1.4% (Illinois No. 6 coal contains 1.6% nitrogen MAF basis). It is very likely that the nitrogen containing compounds in coal derived resid are just as large as the sulfur and oxygen containing compounds. Hence, the effect of increasing macropores of catalyst upon denitrogenation of coal liquids was investigated.

SECTION 4

PROCEDURES, RESULTS AND DISCUSSION

Experiments were carried out in Unit 115. Unit 115 contains two parallel, continuous, fixed bed reactor systems in a single lead bath. Figure 1 is a schematic diagram of one reactor only. Each reactor was fabricated from 1" o.d. by ½" i.d. stainless steel tubing. The volume of catalyst charged to the reactor was 150 cc (compacted). The catalyst bed measured 13" long. A 3-point thermocouple was placed in the reactor to monitor the temperature at the inlet, center, and outlet of the catalyst bed. Heat was supplied to the reactor by means of an electrically heated lead bath designed to maintain isothermal operation which was frequently achieved. However, temperature increases up to 20°F were observed when good performance was achieved.

The catalysts for Runs 115-1255 through 115-1288 were presulfided using a procedure furnished by American Cyanamid. Presulfiding was conducted at operating temperature for 1 hour using 10% H_2S in an H_2 gas mixture supplying more than twice the amount needed to convert the metals to sulfides. A rather time-consuming Armak procedure was followed for later runs numbered 115-1289 through 115-1294. The catalysts were presulfided for 1 hour at 400°F, then another hour at 600°F using the 10% H_2S in H_2 gas mixture. Duplicate runs using these two presulfiding procedures did not show any noticeable difference in catalyst activity.

The experiments were carried out at 780-850°F, 2000-2800 psig, 0.5-1.0 LHSV (volume of feed/hour/volume of catalyst), and excess hydrogen of 4000 SCF/Bbl. A 3-day operation was used for catalyst screening. Longer runs were conducted to assess the deactivation rate of a catalyst when needed. A summary of data from all runs is given in Appendix A.

The feed was pumped to reactor pressure with a metering pump, mixed with hydrogen, and fed to the reactor. The mixed vapor and liquid product from the reactor were cooled and passed to a high pressure receiver. The liquid was let down in pressure and passed to a low pressure receiver. The liquid was let down in pressure and passed to a low pressure receiver. Vent gas was let down in pressure and mixed with flash gas from the low pressure product receiver. The combined gas stream was sampled, metered and vented. The liquid product was collected and weighed periodically. Daily inspection of the liquid product included gravity by hydrometer and nitrogen by Kjeldahl determination. Besides the daily inspection, at the end of 3-day operation, the gas product was analyzed by mass spectrometry, and the liquid product was fractionated. Elemental analyses of C, H, N,

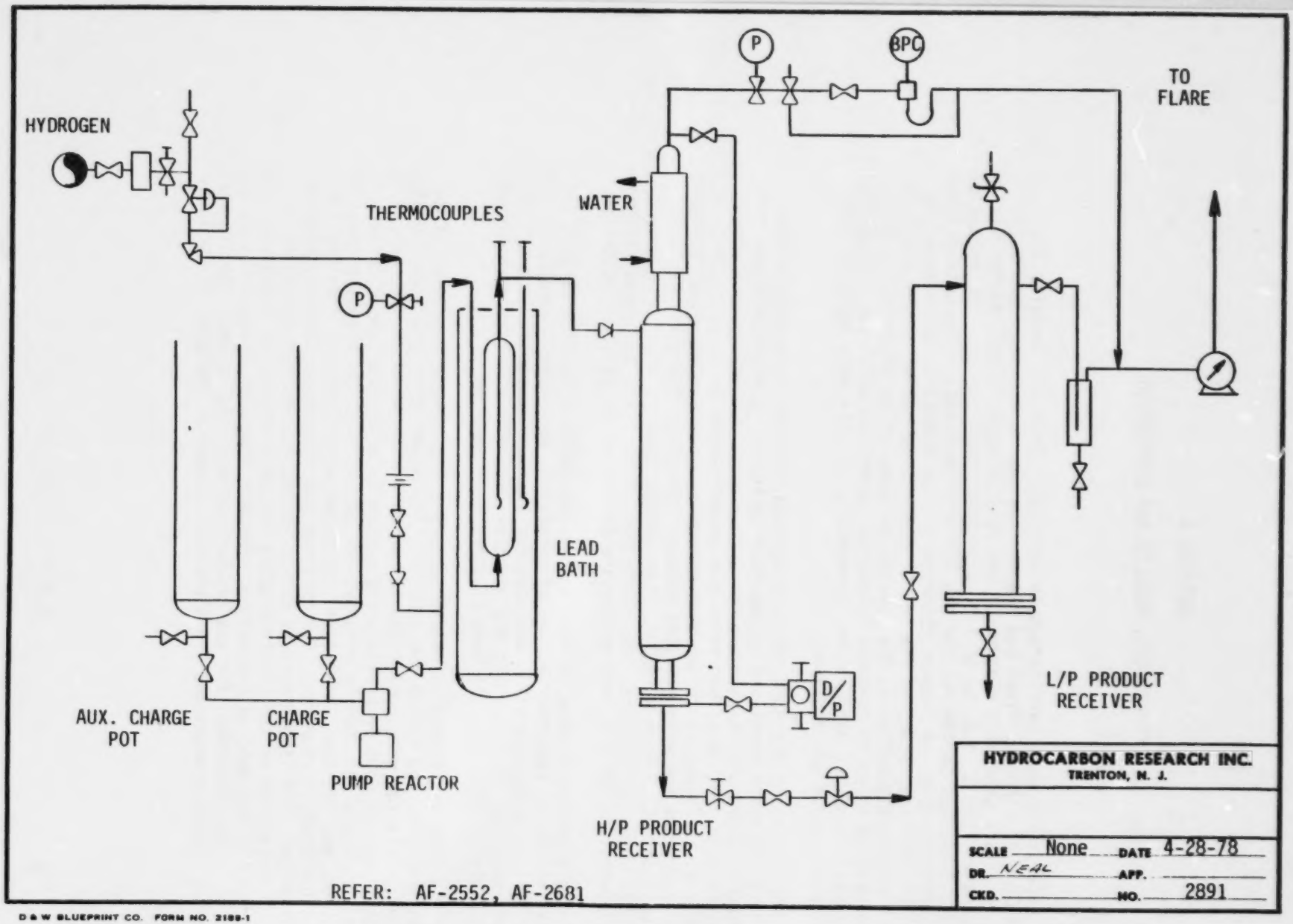

Figure 1. Fixed Bed Denitrogenation Unit - Unit 115

S, O and ash were carried out on the total liquid product, IBP-975^{o}F fraction. The 975^{o}F+ fraction was extracted by benzene or toluene in a Soxhlet extractor for its soluble and insoluble contents. For the 15-day operations, these detailed analyses were conducted on samples taken every three days. Appendix B gives a summary for all runs of operating conditions, product distribution, hydrogen consumption, 975^{o}F+ conversion and heteroatom removal.

A standard shutdown procedure was used upon completion of a run. The temperature was lowered to 650^{o}F, and the catalyst was washed with anthracene oil for 1 hour. A representative sample of the spent catalyst was obtained by riffling. Absorbed material was extracted with benzene or toluene in a soxhlet extractor. The carbon content of the catalyst was determined, and occasionally its nitrogen and sulfur contents were determined. The commercial catalysts and developmental catalysts evaluated in this program were extrudates, 1/16" nominal diameter. Developmental catalysts were prepared by American Cyanamid and Armak.

TASK 1 - DENITROGENATION OF PETROLEUM VACUUM RESID

Gach Saran vacuum resid containing 0.67% nitrogen was used as the feedstock. Inspections of the feedstock are given in Table 1. Since American Cyanamid Co-Mo catalyst HDS 2A has been used for hydroprocessing of resid and coal in this laboratory, it was used as the base catalyst. HDS 9A ni-Mo catalyst, offered by the manufacturer as a good denitrogenation catalyst, was chosen for evaluation.

The characteristics of these two catalysts are described in Table 2; pore size distribution is presented in Figure 2. HDS 2A has a bimodal pore size distribution with macropores in the ranges of 1000 to 7000 Å. HDS 9A has essentially no macropores, and has larger micropores than HDS 2A.

The catalysts were evaluated at conditions favorable for hydrodesulfurization of petroleum resid: 780^{o}F, 2000 psig, 0.75 to 0.40 VHSV. Daily denitrogenation data versus catalyst age are plotted in Figure 3 for a fourteen-day period. Run 115-1255 failed to yield a product containing no more than 0.3% nitrogen, which is the target set by EPA for this program. The target of 0.3 W % nitrogen content was met in run 115-1256, but only at an early catalyst age of 0.1 LB/Bbl, which is unsuitable for equilibrium operations. Deactivation lines like in Figure 3 exist in operations involving hydrodesulfurization of petroleum resid using catalysts possessing similar pore structures.

TABLE 1. FEEDSTOCK INSPECTIONS - GACH SARAN VACUUM RESID

HRI No.		3574	
Fraction	Total	IBP-975	975+
Volume, %	100	4.3	95.7
Gravity, ^{o}API	6.2	16.2	6.0
Sulfur, W %	3.78	2.61	3.84
Carbon, W %	85.15	85.28	85.18
Hydrogen, W %	10.32	11.98	10.65
Nitrogen, W %	0.67	0.27	0.74
Ramsbottom Carbon Residue, W %	19.25		20.31
V, ppm	281	-	-
Ni, ppm	102	-	-

TABLE 2. CHARACTERISTICS OF COMMERCIAL CATALYSTS

Manufacturer	American Cyanamid		Harshaw
	HDS 2A	HDS 9A	HT 400
HRI No.	3556	3687	3779
Composition, W %			
MoO_3	15.1	18.4	14.4
CoO	3.2	-	3.0
NiO	-	3.3	-
SiO_2	0.1	0.7	-
Al_2O_3	Balance	Balance	Balance
Physical Properties			
Compacted Bulk Density, g/cc	0.58	0.82	0.76
Pore Volume, cc/gm	0.67	0.42	0.47
Surface area, m^2/gm	270	150	241
Surface area m^2/cc	403	357	513
Side Crushing Strength, lb/mm	-	-	2.6

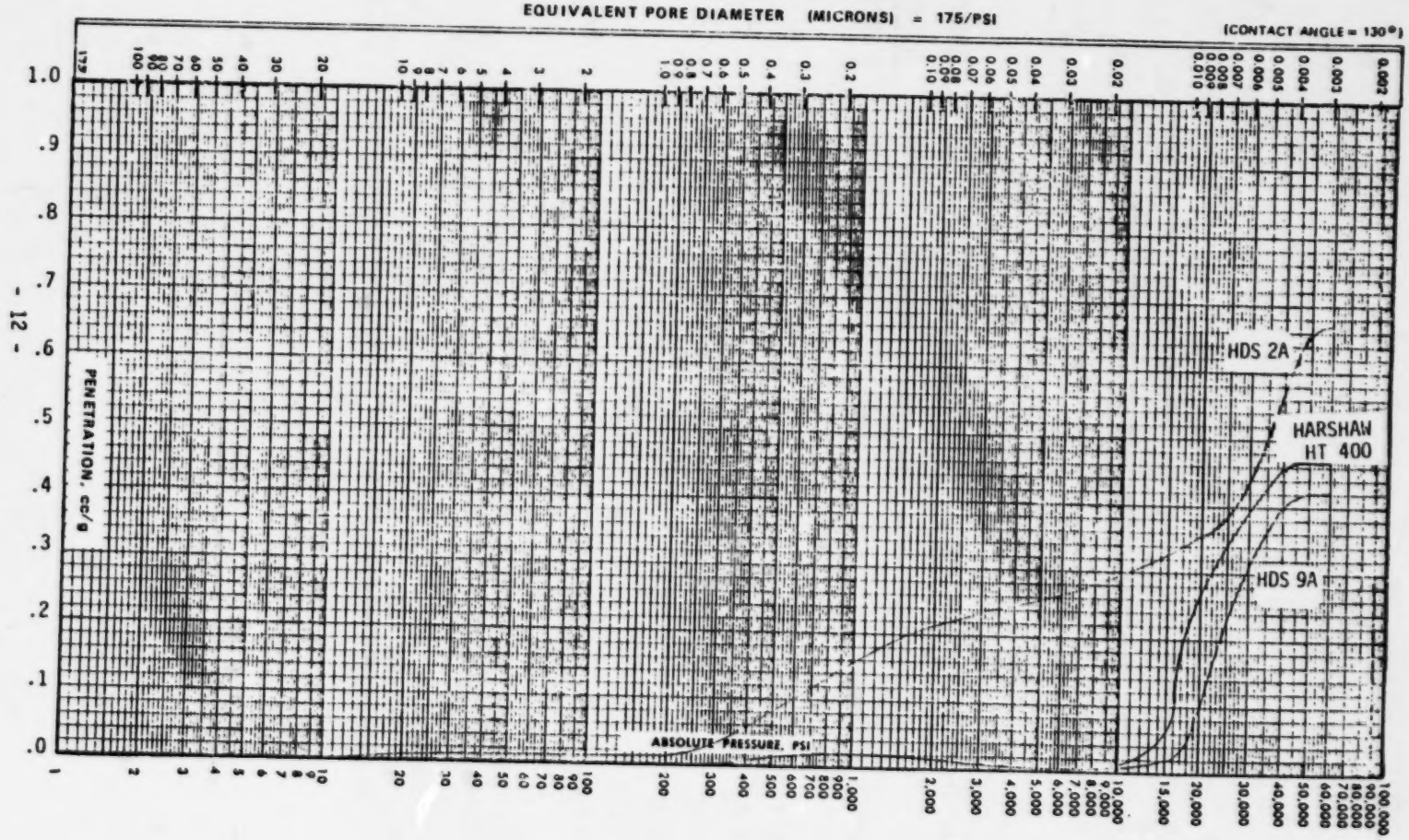

Figure 2. Pore Size Distribution of Commercial Catalysts

LEGEND

	RUN NO.	CATALYST	PRESSURE PSIG	TEMP °F	LHSV	CATALYST SPACE VELOCITY BBL/D/LB
○	115-1255	HDS 2A Co Mo-Al_2O_3	2000	780	0.75	0.10
●	115-1255	HDS 2A Co Mo-Al_2O_3	"	"	0.5	0.05
△	115-1256	HDS 9A Ni Mo-Al_2O_3				
▲	115-1256	HDS 9A Ni Mo-Al_2O_3	2000	780	0.75	0.10
			"		0.40	0.05

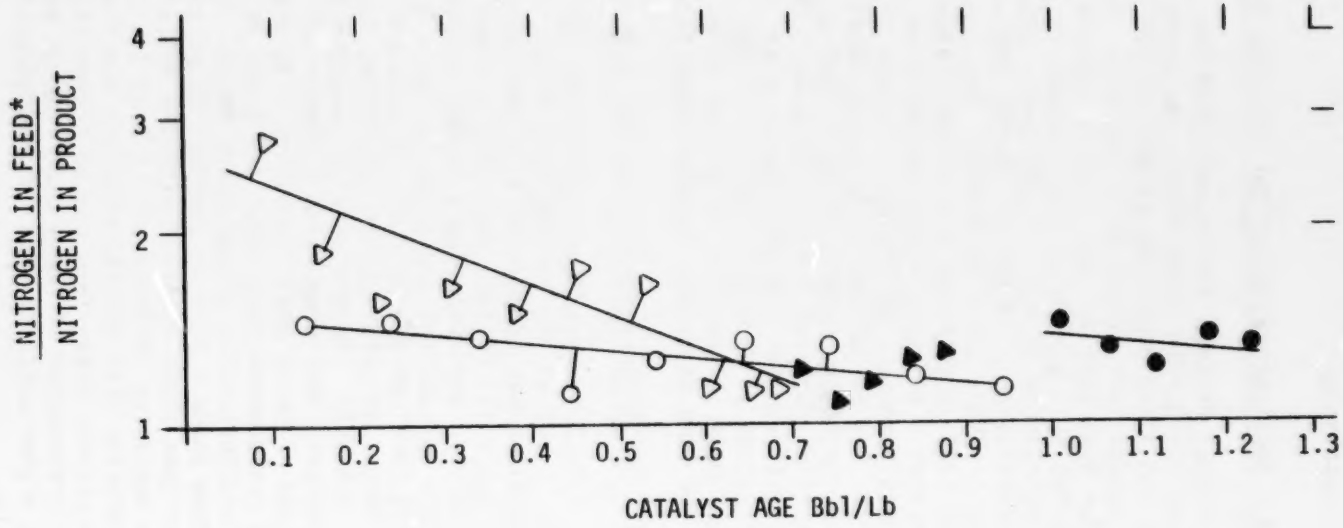

Figure 3. Denitrogenation of Gach Saran Vacuum Resid

*Feed Nitrogen Content = 0.67 W %

TASK 2 - DENITROGENATION OF COAL LIQUIDS FROM H-COAL PROCESS

Four exploratory runs were conducted to evaluate the denitrogenation of a gas oil product and a fuel oil product from the H-Coal process using commercial catalysts.

Subtask 2A - Denitrogenation of Gas Oil from H-Coal Operation

From H-Coal Process Development Unit Run 130-73-13B (coal feed: Illinois No. 6 out of the Burning Star Mine), two drums of atmospheric still bottoms were taken and flash distilled at 500° to 550°F to yield the gas oil feed. Feedstock inspections are given in Table 3. Harshaw HT-400 Co-Mo catalyst was used for Runs 115-1257 and - 1259. Catalyst characteristics are described in Table 2; pore size distribution is shown in Figure 2. The operating conditions of Run 115-1257 and - 1259 were set at favorable hydrodesulfurization conditions: 780°F, 2000-2800 psig, excess hydrogen around 4000 SCF/Bbl, and 2 to 4 VHSV. Run 115-1257 at 2000 psig and 2 VHSV and Run 115-1259 at 2800 and 3 - 4 VHSV yielded about the same extent of denitrogenation. Nitrogen reduction was from 0.45% to an average of 0.09% in the liquid product. At the end of seven days and catalyst age of 1.7 Bbl/lb, there was no noticeable catalyst deactivation. The objective of reducing the nitrogen content of the H-Coal gas oil product to 0.10% for use as a turbine fuel was readily achieved. The carbon content of the spent catalyst from Run 115-1257 operated at 2000 psig was 10.7%, and that from Run 115-1259 at 2800 psig was 8.6%. The lower carbon deposition on the catalyst made it possible to operate at higher space velocity and resulted in the same magnitude of denitrogenation.

Subtask 2B - Denitrogenation of Fuel Oil from H-Coal Operation

From H-Coal Process Development Unit Run 130-73-13B (Coal feed: Illinois No. 6 out of the Burning Star Mine), the naphtha fraction of the settler overflows was topped off in a continuous unit. L-438 was the last portion of the still bottom, and L-440 a blend of the earlier portions. L-438 was heavier and contained a higher percentage of ash than L-440. The feedstock inspections are given in Table 3. Two 3-day runs were conducted using American Cyanamid HDS 2A catalyst. Run 115-1260 was carried out under normal desulfurization conditions for petroleum resid: 780°F, 2000 psig, 0.5 VHSV. Severe catalyst deactivation was at a moderate rate. The data indicate that when using a commercial catalyst such as HDS 2A, denitrogenation of heavy coal liquids to 0.3% nitrogen level will require a catalyst replacement rate about ten times as high as that required for the hydrodesulfurization of petroleum resid. Carbon deposition on spent catalyst from these 2 runs is similar, 20.6% and 19.4% respectively, but much higher than those observed with the H-Coal gas oil feedstock under comparable operating conditions. (8.6 to 10.7% carbon on spent catalyst). The data indicate that initial catalyst deactivation resulted mainly from carbon deposition; heavy feed caused higher carbon deposition than light feed. Denitrogenation of heavy coal liquids needs an improved catalyst possessing higher activity than the hydrodesulfurization catalyst available commercially.

TABLE 3. INSPECTIONS OF FEEDSTOCKS FROM H-COAL PROCESS

	Gas Oil	Fuel Oil	
HRI No.	L 428	L 438	L 440
Gravity, °API	9.5	-12.6	-3.2
Distillation, °F			
IBP	494	412	362
10 V %	523	516	427
30	561	600	682
50	606	750	905
70	671	-	-
90	> 760	-	-
Elemental Composition, W %			
Carbon	88.90	81.05	86.50
Hydrogen	9.28	6.49	7.69
Nitrogen	0.45	0.84	0.81
Sulfur	0.06	0.59	0.37
Oxygen	-	2.28	3.19
Ash	0	5.42	1.72
	98.69	96.67	100.28
Fractions		IBP-945°F	IBP-955°F
V %	-	68	75
Nitrogen, W %	-	0.55	0.47
Sulfur, W %	-	0.17	0.13
Oxygen, W %	-	1.09	2.09
		945°F+*	955°F+**
V %	-	32	25
Nitrogen, W %	-	1.42	1.58
Sulfur, W %	-	1.46	0.90
Oxygen, W %		3.99	3.70
Pour Point, °F	-	130	55
Viscosity, cp			
@ 200°F	-	38	49
@ 300°F	-	24	7.5

*41.6 W %
**32.1 W %

TASK 3 - DEVELOPMENT OF DENITROGENATION CATALYST FOR HEAVY COAL LIQUIDS FROM THE SOLVENT REFINED COAL PROCESS

The objective of this task is to develop an improved denitrogenation catalyst for heavy coal liquid. American Cyanamid Co-Mo catalyst HDS 2A is used as the base catalyst. A blend of 40% SRC product and 60% SRC solvent was used as the feedstock. Task 3 consists of three subtasks. Subtask 1 compared the denitrogenation activity of three metal pairs: Co-Mo, Ni-Mo and Ni-W and two methods of catalyst preparation. Subtask 2 evaluated the effect of the catalyst pore sizes. Subtask 3 evaluated macropores and/or larger micropores than those of the base catalyst.

Preparation of Feedstock

Two drums each of SRC product and solvent were acquired from the Wilsonville Pilot Plant. These two samples were produced from Illinois No. 6 coal from the Monterey Mine. The coal was processed at 835°F, 2400 psig, coal at 38.5 W % concentration in feed slurry, and 25 lb/hr/cu. ft. coal feed rate. Conversion was at 94.7% of MAF feed coal and hydrogen consumption was 3.8 W % of MAF feed coal. A schematic diagram of the Wilsonville Pilot Plant is shown in Figure 4. The product sample was taken from the K-125 product solidifier and the solvent sample from the V-131 recycle solvent storage tank.

Two 450 lb. batches of the SRC blends were prepared. These blends contained 40 W % SRC solids and 60 W % solvent. Inspections of the SRC materials and the feedstock blend are presented in Table 4.

Subtask 3A - Evaluation of American Cyanamid Developmental Catalysts

The objective of this subtask is to compare the denitrogenation performance of Co-Mo, Ni-Mo and Ni-W. Since the method of preparation affects catalyst activity, the same method and support were used in these preparations. The difference given by an impregnation technique and a commercial method of preparation was investigated. The temperature effect and pressure effect upon the Co-Mo and Ni-Mo catalysts were evaluated. The effect of the boiling range of feedstock upon the Ni-Mo catalyst was investigated.

The experimental data lead to the following conclusions:

(1) The commercial method of preparation is superior to the impregnation technique.

(2) Ni-Mo catalyst has higher denitrogenation activity than the Co-Mo or Ni-W catalyst.

(3) Ni-Mo catalyst has the unique feature that it possess higher denitrogenation activity at 810°F than at 850°F. Since low temperature operation leads to low gas-make, this should result in less hydrogen consumption at the same level of denitrogenation.

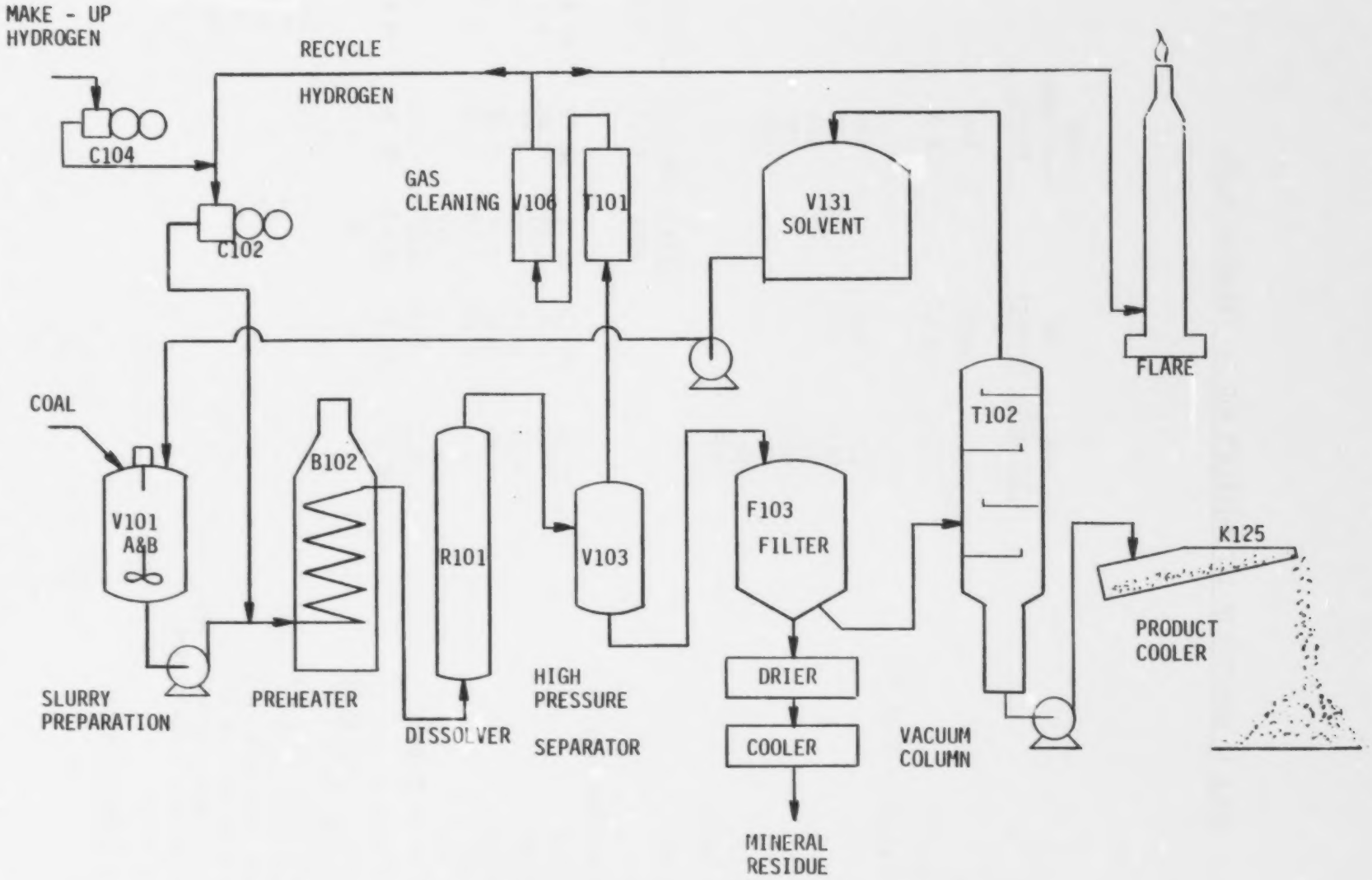

Figure 4. Solvent Refine Coal Process
Wilsonville Pilot Plant

TABLE 4. ANALYSIS OF SRC MATERIALS AND SRC FEEDSTOCK BLEND

	SRC Solvent	SRC Product	SRC Feedstock Blend		
HRI No.	3861	3860	L 446		
Gravity, °API	+1.8	-13.4	-6.8		
Distillation, V % at °F					
IBP	378	700	403		
10	463	945	516		
30	539	-	605		
50	605	-	730		
70	658	-	1000		
90	840	-	-		
End Point	935	-	-		
Fractions			Total	IBP-975°F	975°F+
W %			100%	65.4	34.6
Elemental Analysis, W %					
Carbon,	88.35	86.39	87.76	88.09	87.56
Hydrogen	7.65	5.91	6.80	7.46	5.61
Sulfur	0.67	0.74	0.60	0.77	1.84
Nitrogen	0.69	1.82	1.07	0.32	1.11
Oxygen	-	4.29	3.30	2.32	3.50
Ti, ppm	-	-	115*	-	-
Ash (ASTM Method)	-	0.16	0.09	-	0.03
Total	97.63	99.31	99.62	98.96	99.65
Viscosity, cs at 200°F	-	-	85	-	-
Pour Point, °F	-	-	70	-	-
Benzene-Insoluble, W %	-	-	8.5*	-	24.5
Benzene-Soluble, W %	-	-	26.1*	-	75.5
Toluene-Insoluble, W %	-	-	10.4*	-	30.0
Toluene-Soluble, W %	-	-	24.2*	-	70.0
Ti in Toluene-Insoluble, ppm	-	-	-	-	1000
Ti in Toluene-Soluble, ppm	-	-	-	-	50

* Calculated values

Effect of Active Metals --

American Cyanamid prepared three developmental catalysts for the purpose of evaluating the effect upon denitrogenation of the active metals pairs Co-Mo and Ni-W. The same method and support were used in these preparations. For the sake of expediency, the incorporation of metals was carried out by impregnating the extrudates of γ-alumina support with a solution of the respective metals salts. Commercial catalysts, such as HDS 2A, are prepared differently.

The characteristics of the three developmental catalysts and HDS 2A are summarized in Table 5 in first four columns. These four catalysts have bimodal pore size distributions. The three developmental catalysts have essentially the same pore size distribution. The significant differences between the developmental catalysts and HDS 2A are that the developmental catalysts have higher micropore volume than HDS 2A by 0.2 cc/g and their micropores peak at 100 Å whereas HDS 2A peaks at 50 Å.

Using the same SRC feedstock, HDS 2A catalyst and the three development catalysts were evaluated under the same process conditions, 850°F, 2800 psig, and 0.5 V/Hr/V space velocity. The decline in catalyst denitrogenation activity is shown in Figure 5. Over a catalyst age of three days or about 0.2 Bbl/D/Lb, all four catalysts show definite deactivation. The commercial Co-Mo catalyst HDS 2A is the most stable one. The Co-Mo development catalyst has slightly higher initial activity and the highest deactivation rate. These differences in performance are attributed to the differences in the method of preparation and not to the differences in the pore size distribution. The effect of active metal shown by the three developmental catalysts indicates that Ni-Mo is better for denitrogenation than the Co-Mo and Ni-W. These preliminary indications were later followed up by the evaluation of a Ni-Mo catalyst prepared by the same method used for the commercial catalyst HDS 2A. (discussed on page 22).

The carbon contents of the spent catalysts were very high, 27 to 39%. In hydroprocessing of petroleum residuum and coal, carbon deposition on this type of catalyst is 10 to 20%.

Effect of Method of Catalyst Preparation --

Five additional Co-Mo catalysts and Ni-Mo catalysts were furnished by American Cyanamid. These catalysts were prepared in the laboratory using the same method as that for HDS 2A. These catalysts were evaluated to ascertain whether the method of preparation can be an important variable affecting catalyst activity and whether Ni-Mo is indeed better for denitrogenation than Co-Mo. The characteristics of these five developmental catalysts are described in the five right hand columns of Table 5. The two additional Co-Mo catalysts, HRI 3866 and HRI 3867, have similar total pore volume and similar pore size distribution as the first Co-Mo developmental catalyst HRI 3849, but slightly more micropores than catalyst HDS 2A. The Ni-Mo catalysts vary more in their pore size distribution.

TABLE 5. CHARACTERISTICS OF AMERICAN CYANAMID DEVELOPMENTAL CATALYSTS

Catalyst HRI No.	3556	3849	3850	3851	3866	3867	3904	3905	3911
American Cyanamid No.	HDS 2A	SN 4412B	SN 4412A	SN 4412C	SN 4424	SN 4425	SN 4474	SN 4475	SN 4510
Active Metals	Co-Mo	Co-Mo	Ni-Mo	Ni-W	Co-Mo	Co-Mo	Ni-Mo	Ni-Mo	Ni-Mo
Composition, %									
CoO	3.2	3.2	-	-	3.2	3.2	-	-	-
NiO	-	-	3.2	3.2	-	-	3.5	3.5	3.2
MoO_3	15.1	15.5	15.5	-	14.4	14.1	15.9	17.2	15.3
WO_3	-	-	-	15.5	-	-	-	-	-
SiO_2	0.1	-	-	-	0.06	0.05	-	-	1.2
Na_2O	-	-	-	-	0.01	0.01	0.017	0.015	0.05
SO_4	-	-	-	-	0.2	0.2	0.3	0.3	0.2
P_2O_5	-	3.5	3.5	-	-	-	-	-	-
Physical Properties									
Diameter, mm	1.68	1.65	1.65	1.65	1.68	1.68	1.63	1.63	1.52
Length, mm	5	9.9	10.9	8.6	5.1	5.3	5.1	5.1	4.3
Pore Volume, cc/g	0.67	0.82	0.83	0.89	0.83	0.85	0.69	0.72	0.50
Surface Area, m^2/g	270	195	204	237	339	280	335	267	305
CBD, g/cc	0.58	0.54	0.54	0.51	0.53	0.54	0.61	0.60	0.75
Side Crush Strength, lb/mm	-	2.4	1.9	2.5	3.1	3.8	2.8	1.5	4.9
Pore Size Distribution by H_g Porosimeter									
PV cc/g <200Å dia	0.43	0.54	0.55	0.60	0.53	0.53	0.43	0.44	0.494
200 -1500Å	0.10	0.12	0.11	0.12	0.10	0.12	0.09	0.08	0
>1500Å	0.14	0.16	0.17	0.17	0.19	0.20	0.17	0.20	0.02
Total	0.67	0.82	0.83	0.89	0.83	0.85	0.69	0.72	0.496

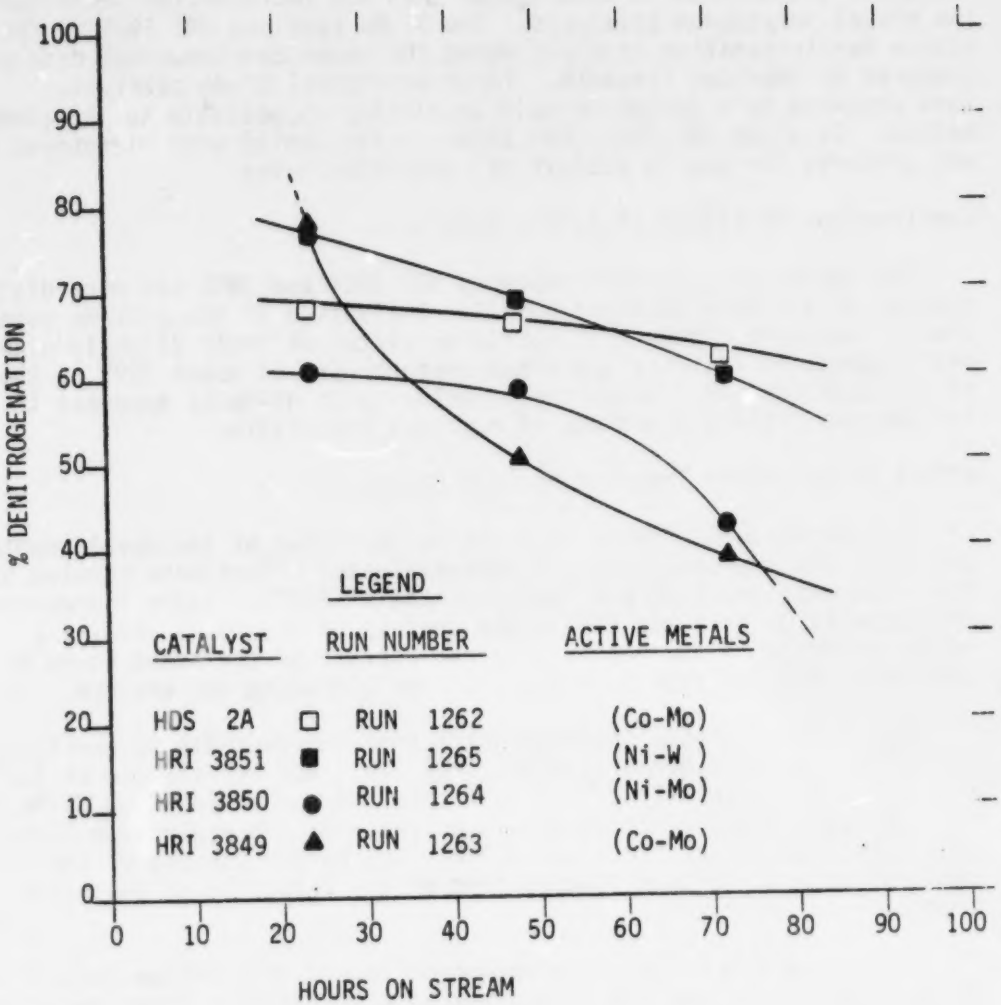

Figure 5. Comparison of Denitrogenation Activity Among Three Developmental Catalysts and HDS 2-A

Table 6 summarizes the pertinent catalyst characteristics and denitrogenation data of the developmental catalysts and the base catalyst. The commercial method of preparation was better than the impregnation method as shown by the higher denitrogenation activity of the two developmental Co-Mo catalysts compared with that of HRI 3849. The commercial method of preparation is also better than the impregnation technique for the nickel-molybdenum catalysts. The Ni-Mo catalyst HRI 3905 is the most active denitrogenation catalyst among the seven developmental catalyst prepared by American Cyanamid. Three additional Ni-Mo catalysts were prepared by a technique held as closely as possible to the commercial method. Catalyst HRI 3911 (not shown in the table) with micropores only was prepared for use in Subtask 3B, described later.

Confirmation of Effect of Active Metals--

The two Ni-Mo catalysts numbered HRI 3904 and 3905 had pore distributions similar to the base catalyst HDS 2A. Evaluation of these Ni-Mo catalysts showed they were better than HDS 2A by virtue of their slightly higher denitrogenation activity and a temperature rise of about 15°F at the inlet of the catalyst bed. Hence the superiority of Ni-Mo is apparent in the data for the two different methods of catalyst preparation.

Effect of Operating Temperature upon Catalysts--

The temperature effects upon the performances of the developmental catalysts and the base catalyst were evaluated. Runs were carried out at lower temperature, 810° and 780°, instead of 850°F. Table 7 presents the denitrogenation data and the carbon content of the spent catalysts. A 10 to 15% decrease in the absolute carbon content of the spent Co-Mo or Ni-Mo catalysts resulted from a decrease of the operating temperature.

The Ni-Mo catalysts showed significance improvements in denitrogenation at 810°F. The best Ni-Mo catalyst, HRI 3905, was reevaluated at 810°F to show the reproducibility of the test data. A run at 780°F on Ni-Mo catalyst HRI 3850 gave lower denitrogenation activity at the end of the 3-day operation than were obtained at 810°F and 850°F. The carbon content of the spent catalyst was not further lowered through the reduction of operating temperature from 810° to 780°F.

To achieve a certain denitrogenation level, this unique feature of Ni-Mo catalyst enables one to operate at significantly lower temperature than that for the Co-Mo catalyst. This would yield less gas, and thus results in less hydrogen consumption.

Effect of Operating Pressure Upon Catalysts--

The pressure effect upon the Co-Mo, Ni-Mo, and Ni-W catalysts was evaluated Runs 115-1275, - 1276, - 1277, - 1278 were conducted at 810°F, 2000 psig, and 0.5 VHSV. The denitrogenation data as shown in Table 8 were rather scattered. The Ni-Mo catalyst definitely showed lower denitrogenation activity at lower pressure accompanied by higher carbon deposition on the catalyst. In the case of Co-Mo and Ni-W catalysts, the pressure effect was less significant.

TABLE 6. EVALUATION OF METHOD OF PREPARATION

Catalyst							
HRI No.	3849	3556	3866	3867	3850	3904	3905
American Cyanamid No.	SN 4412B	HDS 2A	SN 4424	SN 4425	SN 4412A	SN 4474	SN 4475
Active Metals	Co-Mo				Ni-Mo		
Preparation	Impregnation	Commercial*			Impregnation	Commercial*	
Pore Volume, cc/g							
Total	0.82	0.67	0.83	0.85	0.83	0.69	0.72
< 200 Å	0.54	0.43	0.53	0.53	0.55	0.43	0.44
200-1500 Å	0.12	0.10	0.10	0.12	0.11	0.09	0.08
> 1500 Å	0.16	0.14	0.19	0.20	0.17	0.17	0.20
% Denitrogenation at	850°F, 2800 psig, 0.5 VHSV						
Run No. 115 -	1263	1262	1283	1284	1264	1281	1282
Period 1B	77.5	68.5	74.9	72.1	76.8	74.3	61.9
2B	50.2	66.8	65.2	78.7	68.6	56.4	59.1
3B	39.0	62.7	34.7	69.7	59.7	69.6	69.1

*NOTE: Catalysts prefixed by an "SN" before the number are developmental catalysts, even though some were prepared using commercial methods.

TABLE 7. TEMPERATURE EFFECT UPON HYDROGENITROGENATION OF SRC LIQUIDS

Catalyst						
HRI No.	3556	3866	3867	3850	-----3905 ----------	
American Cyanamid No.	HDS 2A	SN 4424	SN 4425	SN 4412A	----SN 4475----------	
Active Metals	---------- Co-Mo----------				----Ni-Mo----------	
Preparation Method	------Commercial Method----------			Impregnation	-----Commercial Method--	
% Denitrogenation at	850°F, 2800 psig, 0.5 VHSV					
Run No. 115 -						
Period 1B	1262	1283	1284	1264	1282	
2B	68.5	74.9	72.1	76.8	61.9	
3B	66.8	65.2	78.7	68.6	59.1	
Spent Catalyst, % C	62.7	34.7	69.7	59.7	69.1	
	30.1	35.7	31.0	31.9	28.5	
% Denitrogenation at	810°F, 2800 psig, 0.5 VHSV					
Run No. 115 -						
Period 1B	1266	1270	1271	1267	1280	1285
2B	64.9	76.1	63.0	76.7	80.4	79.6
3B	46.6	70.9	63.6	75.9	82.5	74.4
Spent Catalyst, % C	50.5	63.0	65.5	65.9	72.1	70.2
	25.3	22.7	24.2	21.5	23.3	24.3
% Denitrogenation at	780°F, 2800 psig, 0.5 VHSV					
Run No. 115 -						
Period 1B	1269					
2B	78.3					
3B	75.0					
Spent Catalyst, % C	40.3					
	23.1					

TABLE 8. EFFECT OF PRESSURE ON HYDRODENITROGENATION OF SRC LIQUIDS

Catalyst				
HRI No.	3556	3849	3850	3851
American Cyanamid No.	HDS 2A	SN 4412B	SN 4412A	SN 4412C
Active Metals	Co-Mo	Co-Mo	Ni-Mo	Ni-W
% Denitrogenation at	2800 psig, 810°F, 0.5 VHSV			
Run No. 115 -	1266	1273*	1267	1274*
Period 1B	64.9	44.0	76.8	45.1
2B	46.6	70.3	68.6	50.2
3B	50.5	49.1	59.7	35.0
Spent Catalyst, % C	25.3	24.2	21.5	15.8
% Denitrogenation, at	2000 psig, 810°F, 0.5 VHSV			
Run No. 115 -	1275	1277	1276	1278
Period 1B	37.9	65.2	36.2	50.7
2B	59.9	68.3	53.9	40.9
3B	43.9	54.8	61.9	41.1
Spent Catalyst, % C	26.2	23.6	30.4	21.1

* After presulfiding, the catalyst was held accidentally under hydrogen atmosphere for 9 hours at 810°F prior to the start of feed. This might reduce the catalyst and result in low denitrogenation activity.

Effect of Feed Upon Ni-Mo Catalysts --

From the experiments conducted under Task 2, using H-Coal gas oil product and H-Coal fuel oil product, it was observed that heavy feed caused higher carbon deposition resulting in faster catalyst deactivation than with lighter feed. Run 115 - 1268 was carried out using the SRC solvent with boiling range comparable to that of H-Coal gas oil and Ni-Mo catalyst HRI 3850. No catalyst deactivation was observed during the 3-day operation. There was low carbon deposition on the catalyst, viz., 10.7% vs 23.1% from Run 115-1269 using the SRC blend feedstock under same operating conditions.

Subtask 3B - Evaluation of the Significance of Bimodal Pore Size Distribution of Ni-Mo Catalyst

After Ni-Mo was found to be more effective in denitrogenation than Co-Mo, American Cyanamid was requested to prepare a Ni-Mo catalyst having micropores only. The other variables, such as method of preparation, support, and metal contents were to be the same as that of catalyst HRI 3905. The characteristic of this catalyst, HRI 3911 was included in Table 5. Pore size distribution of HRI 3905 and HRI 3911 is shown in Figure 6. HRI 3911 has only 0.5 cc/g total pore volume versus 0.7 cc/g for HRI 3905. i.e., HRI 3911 has higher density. With a charge of 150 cc catalyst volume, 118g of HRI 3911 are charged to the reactor vs. 90g of HRI 3905.

As shown in Table 9, HRI 3911 (Run 115-1286) has only an average of 4% higher denitrogenation activity for the 3-day operation than that shown by HRI 3905 in Runs115-1280 and 1285. This is true even though Run 115-1286 using HRI 3911 had a mugh higher weight of catalyst than Runs 115-1280 and - 1285 using HRI 3905. The data indicate that the presence of macropores in HRI 3905 increases the denitrogenation activity of the catalyst significantly on a catalyst weight basis. The presence of macropores in HRI 3905 probably allows the denitrogenation reactions to be less diffusion limited. The result supports the expectation that by enlarging the macropores and/or the micropores of a catalyst, its denitrogenation activity will be improved.

Subtask 3C - Optimization of the Bimodal Pore Size Distribution of Ni-Mo Catalyst

Description of Catalysts --

For the last part of the program, development was sought of an improved denitrogenation catalyst. Armak was subcontracted to prepare four Ni-Mo catalysts with larger macropores and/or larger micropores. They were to maintain the same total pore volume (0.7 cc/g)and the same pore volume distribution between the macropores and micropores (about 1/3 in macropores and 2/3 in micropores).

The technology is available for enlarging the micropores from the 50 Å range to 100 Å range, but not for enlarging the macropores. Armak undertook extrusion research to develop a technique for increasing and enlarging the macropores with limited success. The characteristics of the four Armak catalysts and American Cyanamid catalyst HRI 3905 are described in Table 10. The pore size distribution of these four catalysts and American Cyanamid

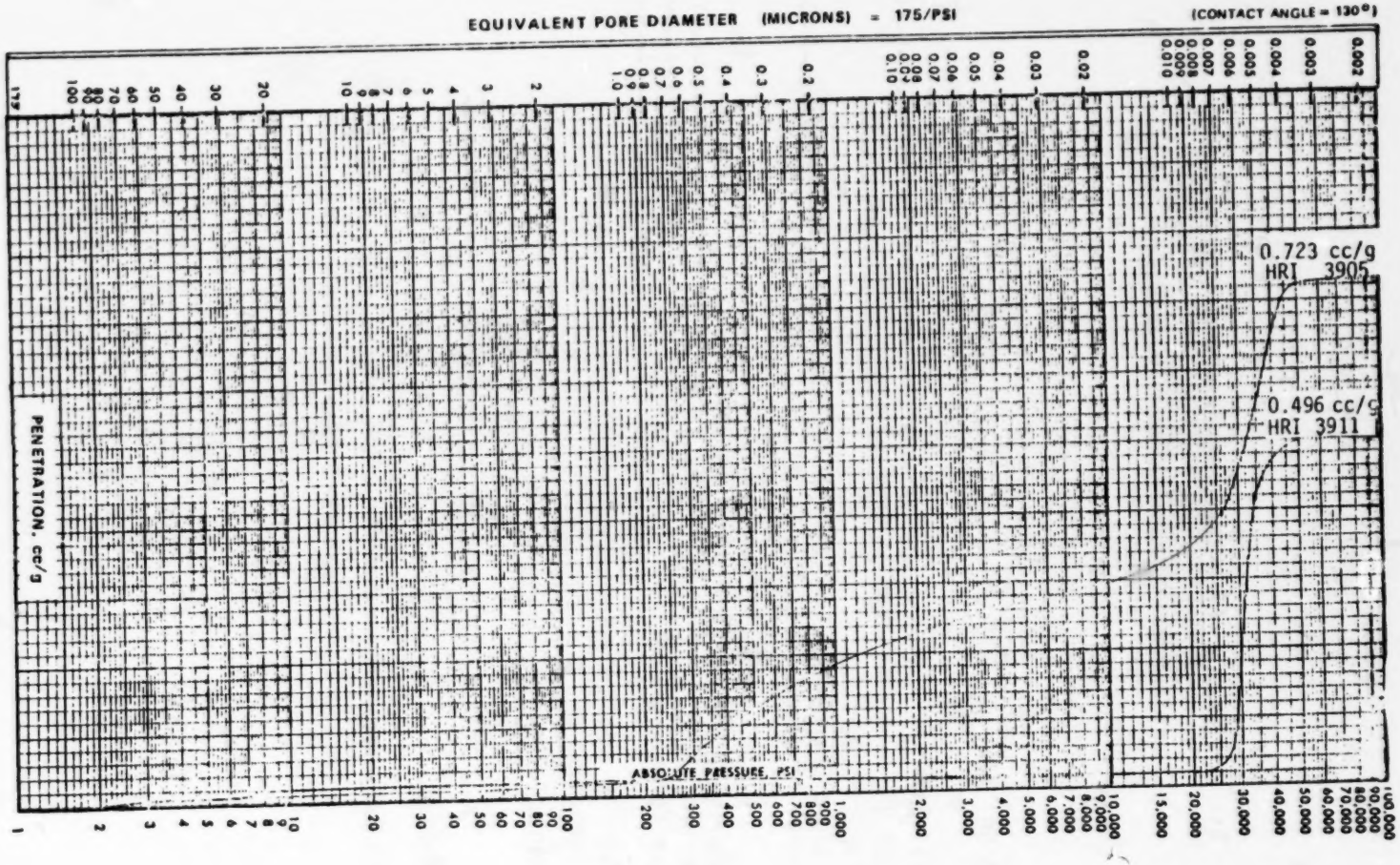

Figure 6. Pore Size Distribution of Nickel-Molybdate Catalysts

TABLE 9. EFFECT OF MACROPORES IN CATALYST UPON DENITROGENATION OF HEAVY COAL LIQUIDS

Run No. 115 -	1280	1285	1286
Catalyst	----------Ni-Mo----------		
HRI No.	----------3905------		3911
Pores >1500 Å	----------0.20------		0.02
Volume Charged, cc	----------150----------		
Weight Charged, g	90.4	89.5	118.4
Temperature, °F	---------- 810----------		
Pressure, psig	----------2800----------		
Space Velocity, V/Hr/V	----------0.5----------		
Denitrogenation, %			
Period 1B	80.4	79.6	81.5
2B	82.5	74.4	79.0
3B	72.1	70.2	78.8
Average	78.3	74.7	79.8
Spent Catalyst, % C	23.3	24.3	22.1

TABLE 10. CHARACTERISTICS OF Ni-Mo CATALYSTS

HRI No.	3905	3922	3928	3959	3966
Manufacturer	Am. Cy.	Armak			
No.	SN 4475	PA 24268	PA 24266	PA 25137	PA 24738
Composition					
NiO, %	3.5	3.2	3.2	3.3	4.2
MoO_3, %	17.2	14.0	14.1	15.3	19.5
SiO_2, %	-	0.74	0.48	0.37	0.4
Na_2O, %	0.015	0.04	0.03	0.06	0.03
SO_4, %	0.3	0.91	0.40	0.12	<0.2
Physical Properties					
Diameter, mm	1.63	1.84	1.65	1.71	-
Length, mm	5.1	-	-	-	-
Pore Volume, cc/g	0.72	0.48	0.61	0.64	0.71
Surface Area, m^2/g	267	206	243	139	116
Surface Area, m^2/cc	158	167	165	95	68
Compacted Bulk Density, g/cc	0.60	0.79	0.66	0.68	-
Reactor Density, g/cc	0.60	0.81	0.68	0.68	0.59
Side Crush Strength, lb/mm	1.5	1.5	2.8	0.9	<< 1
Pore Size Distribution by Hg Porosimeter					
PV cc/g < 200Å dia.	0.45	0.38	0.35	0.37	0.21
200-2000Å	0.10	0.02	0.09	0.10	0.17
> 2000Å	0.17	0.08	0.17	0.17	0.33
Total	0.72	0.48	0.61	0.64	0.71

Ni-Mo catalyst HRI 3905 is presented in Figure 7.

Armak catalyst HRI 3928 has a pore size distribution roughly like that of American Cyanamid catalyst HRI 3905. It has higher density and its pore volume is lower by 0.11 cc/g with 1/3 of the pore volume loss occurring in the 500-3000 Å range and 2/3 in the 30 to 100 Å range. Armak catalyst HRI 3959 has a bimodal pore size distribution with the micropores shifted from around the 50 Å range to 100 Å and its pore volume is 0.08 cc/g lower than HRI 3905. Armak catalyst HRI 3922 has the highest density and lowest pore volume (0.48 cc/g) among the five catalysts. It lacks medium size pores and its micropores are similar to those of HRI 3905. Armak catalyst HRI 3966 is the only catalyst possessing significantly more and larger macropores. Its micropores are around 110 Å occupy less than half of the pore volume as do the micropores in HRI 3905.

Armak Catalyst Preparations--

A brief description of catalyst preparation techniques was furnished by Armak. Catalyst HRI 3922 was prepared by impregnating the extrudates of the alumina support. The other three catalysts were prepared differently. Mo was incorporated by mixing the wet solids. After extrusion, Ni was impregnated onto the extrudates. The Mo-containing extrudates of catalyst HRI 3966 had high total pore volume. In order to meet our specifications of increasing the size and quantity of macropores but keeping the same total pore volume as that of American Cyanamid catalyst HRI 3905, Armak calcined the extrudates at high temperature to reduce the quantity of micropores prior to Ni impregnation. This resulted in a weaker catalyst and might have adverse effect upon catalyst activity.

Evaluation of Armak Catalysts--

The four Armak catalysts were evaluated in 3-day runs, at 810°F, 2800 psig and 0.5 VHSV. Catalyst HRI 3966 was evaluated at two space velocities, 0.5 and 1.0 V/Hr/V, and the operations were continued for 15 days. Table 11 summarizes the pertinent data for the 3-day operations on the four Armak catalysts and American Cyanamid catalyst HRI 3905. Triplicate runs were conducted on HRI 3928 and HRI 3905 under the same operating conditions to show the precision of denitrogenation data.

Catalyst HRI 3928 with lower macropore volume and micropore volume than HRI 3905 had slightly lower denitrogenation activity on the catalyst volume basis. The difference was more pronounced on the catalyst weight basis. High density catalyst HRI 3922 has much lower macropore volume than HRI 3905, 0.10 vs. 0.27 cc/g for > 200 Å dia. as shown in Table 11. Their initial denitrogenation activities during the 3-day operation are about the same on catalyst volume basis; however, the weight of HRI 3922 charged to the reactor is 35% higher than that of HRI 3905. Since both the catalyst age and catalyst cost are on weight basis, HRI 3905 is the superior catalyst among these three.

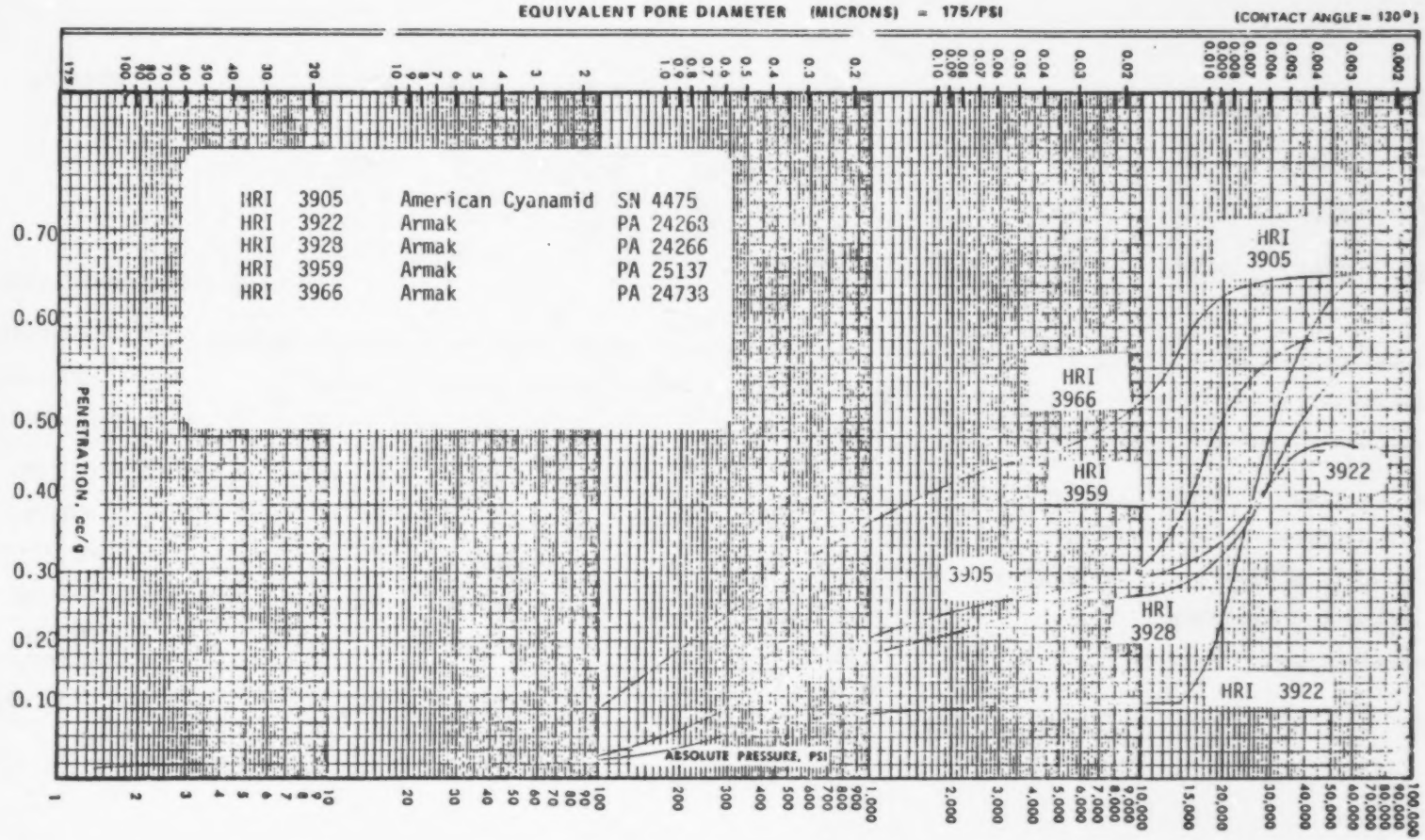

Figure 7. Pore Size Distribution of Nickel-Molybdate Catalysts

TABLE 11. COMPARISON OF ARMAK CATALYSTS AND AMERICAN CYANAMID CATALYST HRI 3905

Run No. 115-	1288	1290	1291	1287	1292	1293	1294	1280	1285	1289
Catalyst HRI No.	3928			3922	3959	3966		3905		
Manufacturer	Armak							American Cyanamid		
No.	PA 24266			Pa 24268	PA 25137	PA 24738		SN 4475		
Volume Charged, cc	150						75	150		
Weight Charged, g	101.7	101.8	102.0	122	101.5	88.1	43.3	90.4	89.5	88.9
Temperature, °F	810									
Pressure, psig	2800									
Space Velocity, V/Hr/V	0.5						1.0	0.5		
Denitrogenation, W %										
1B	67.9	70.4	61.2	-	83.7	83.5	54.5	80.4	79.6	85.9
2A	81.2	-	68.9	65.4	80.1	81.8	52.0	-	-	-
2B	74.6	65.8	74.7	75.1	84.0	75.5	48.9	82.5	74.4	77.9
3A	73.7	-	63.4	79.4	73.6	-	-	-	-	-
3B	69.7	62.8	78.9	73.6	73.4	76.6	53.8	72.1	70.2	72.9
Average	73.4	66.3	69.4	73.4	78.8	79.4	52.3	78.3	74.7	78.9

HRI 3959 and HRI 3928 are similar in every respect, including the catalyst preparation technique, except that the micropores of HRI 3959 are around 100 Å vs. 50 Å for HRI 3928. HRI 3959 has moderately higher denitrogenation activity than HRI 3928. It is concluded that increasing the micropore sizes of a catalyst increases its denitrogenation activity moderately. However HRI 3959 does not show better denitrogenation activity than HRI 3905, which has micropores as small as those of HRI 3928. This can be attributed to two possibilities: HRI 3905 has 0.08 cc/g more pore volume in micropores than HRI 3959; or the method of preparing HRI 3905 is better than the method for HRI 3959.

The Ni-Mo catalyst HRI 3966 is very high in macropore volume and has 0.13 cc/g pore volume of pores > 1000 Å It also has large micropores (100 Å range). Its denitrogenation activity is about the same as that of HRI 3959. The data seem to indicate that increasing macropores at the expense of the micropores does not increase the denitrogenation activity of the catalyst. However, as stated above, HRI 3966 was calcined at high temperature. This deviation from the regular method of preparation may have an adverse effect on the catalyst activity.

HRI 3966 has the lowest surface area. As shown in Table 10, the surface area of HRI 3966 is only 68 m^2/cc versus 95 to 167 m^2/cc for the other four catalysts. Theoretically, less surface area needs less metals for covering the catalyst support. HRI 3966 probably can be made into a version containing substantially less Ni and Mo. If the denitrogenation activity is not decreased, a low cost catalyst may result.

Effect of Space Velocity--

The Ni-Mo catalyst HRI 3966 was evaluated at 2 space velocities, 0.5 and 1.0 V/Hr/V, over a 15-day period. For Run 115-1294, to achieve 1.0 V/Hr/V, the catalyst was diluted with an equal volume of carborundum. The catalyst deactivation data are plotted in Figure 8. The effect of space velocity is rather unexpected. As shown in Figure 8, at 0.7 bbl/lb catalyst age, Run 115-1293 at 0.5 VSHV shows a steep deactivation, whereas Run 115-1294 at 1.0 LHSV does not. A line through these later data for 0.5 LHSV would cross the line for the data at 1.0 VHSV at a catalyst age of 0.8 bbl/lb.

LEGEND	RUN NO.	CATALYST	PRESSURE, PSIG	TEMP, °F	LHSV	CATALYST SPACE VELOCITY, BBL/LB
▲	115-1293	HRI 3966	2800	810	0.5	0.058
■	115-1294	HRI 3966	2800	810	1.0	0.116

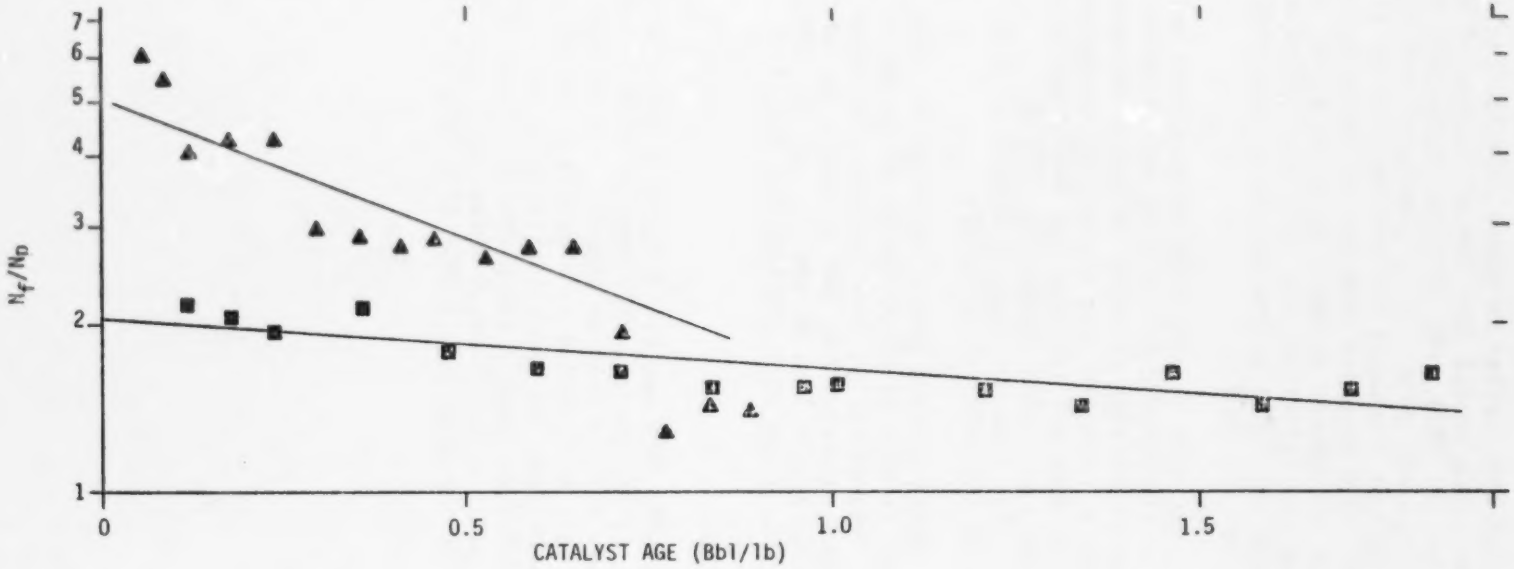

Figure 8. Denitrogenation of SRC Blend

Semi-quantitative emission spectrographic analysis of the used catalyst from Run 115-1293 is presented in Table 12. The major metal contaminants were boron, titanium and iron. Quantitative analyses of the contaminants on the used catalyst from Run 115-1293 and - 1294 are tabulated below:

	Spent Catalyst	
Run No.	115-1293 (.5 VHSV)	115-1294 (1.0 VHSV)
Carbon, W %	26.6	17.7
Hydrogen, W %	1.15	0.90
Sulfur, W %	6.01	6.28
Nitrogen, W %	0.58	0.46
Ti, W %	0.31	0.31

These two used catalysts had about the same amount of hydrogen, sulfur and nitrogen. Titanium deposition on the catalyst amounted to only about 18.3% of the titanium present in the SRC feedstock. Carbon content of the spent catalyst from Run 115-1293 was significantly higher than that from Run 115-1294, 26.6% versus 17.7%. Run 115-1293 had significantly higher 975^{o}F+ conversion than Run 115-1294 over the first 6-day operation, an average of 65% versus 49% conversion. It is likely that operating at lower space velocity gives deeper resid conversion. This results in higher carbon deposition on the catalyst which leads to steeper catalyst deactivation.

TABLE 12. EMISSION SPECTROGRAPHIC ANALYSIS OF USED CATALYST FROM RUN 115 - 1293

Element	Percent
Aluminum	>10
Molybdenum	>10
Nickel	1-10
Boron	0.9
Silicon	0.5
Titanium	0.5
Iron	0.4
Manganese	0.007
Magnesium	0.04
Lead	0.005
Chromium	0.015
Vanadium	0.05
Bismuth	0.005
Copper	0.07
Silver	0.01
Cobalt	0.001

APPENDIX A

SUMMARY OF RUN DATA

DENITROGENATION OF PETROLEUM VACUUM RESID

Run No. / Period	Catalyst HRI No.	Catalyst Mfr's No.	Feed	Temp °F	Pressure psig	Space Velocity V/Hr/Vc	Space Velocity B/D/Lb	Excess H_2 SCF/Bbl	Cat. Age Bbl/Lb	Liquid Product °API	Liquid Product % N	Liquid Product % S
Unit 115	3556	American Cyanamid HDS 2A Co-Mo on Al_2O_3, 1/16" extra -dates	Gach Saran Vacuum Resid 6.2 °API 0.67 % N 3.78 % S									
1255-1B				774	1985	0.86	0.103	6108	0.138	13.5	0.462	1.94
2				774	1985	0.84	0.101	5642	0.239	13.3	0.456	1.84
3				779	1950	0.86	0.103	6149	0.342	14.2	0.501	1.81
4				776	1950	0.87	0.104	7102	0.446	13.3	0.607	1.88
5				776	1960	0.84	0.101	5403	0.547	12.5	0.542	1.90
6				776	1980	0.84	0.101	5133	0.648	14.4	0.508	2.00
7				777	1985	0.88	0.106	4658	0.745	11.0	0.510	2.44
8				778	1995	0.82	0.099	5533	0.844	10.4	0.563	2.20
9				782	1990	0.82	0.099	5056	0.943	9.7	0.604	2.10
10				780	2000	0.54	0.065	3666	1.008	13.9	0.466	1.88
11				781	2000	0.47	0.056	6730	1.064	14.3	0.515	1.68
12				780	1995	0.48	0.058	3867	1.122	17.6	0.553	1.86
13				776	1990	0.48	0.058	3751	1.180	13.9	0.488	2.04
14				779	2005	0.46	0.055	4467	1.235	12.6	0.513	1.92
1256-1B	3687	American Cyanamid HDS 9A Ni-Mo on Al_2O_3 Trilobe	Gach Saran Vacuum Resid	782	2010	0.86	0.073	4174	0.093	18.5	0.244	0.85
2				780	1995	0.75	0.064	5108	0.157	18.8	0.361	0.78
3				785	1995	0.82	0.070	4388	0.227	18.2	0.442	0.80
4				785	2010	0.93	0.079	3717	0.306	16.7	0.415	1.21
5				780	2015	0.90	0.077	4200	0.383	15.6	0.449	1.53
6				778	2000	0.81	0.069	4332	0.457	17.2	0.387	1.91
7				780	2020	0.86	0.073	4382	0.535	12.8	0.412	2.24
8				779	2015	0.84	0.071	4426	0.606	12.3	0.601	2.47
9				782	2000	0.82	0.069	4332	0.675	11.6	0.597	2.58
10				780	2000	0.51	0.043	4402	0.718	14.9	0.557	2.39
11				780	1990	0.44	0.038	4421	0.756	14.3	0.621	2.42
12				780	2000	0.43	0.037	4529	0.795	15.5	0.583	2.69
13				776	2000	0.51	0.043	4734	0.838	14.4	0.544	2.85
14				780	1995	0.42	0.035	4692	0.873	13.2	0.531	2.87

DENITROGENATION OF COAL LIQUIDS FROM SOLVENT REFINED COAL PROCESS

Run No.- Period Unit 115	HRI No.	Mfr's Iden. No.	Feed	Temp. °F	Pressure Psig	Space Velocity V/Hr/V	Space Velocity B/D/Lb	Excess H_2 Bbl/Lb	Cat. Age Bbl/Lb	H_2 Consumption SCF/Bbl	H_2 Consumption W %	Liquid Product W % Output Basis	Liquid Product °API	Liquid Product % N	Liquid Product 975°F+ W %	Spent Catalyst, % C
1257-1B	3779	Harshaw	H-Coal	781	2015	2.12	0.183	3950	0.149	1165	1.75	99.8	17.0	0.097	-	
2A		HT-400	Gas Oil	780	2010	2.00	0.172	3920	0.220	1065	1.60	99.7	16.4	0.088	-	10.7
		Co-Mo on Al_2O_3	Pdt L428 9.5 °API 0.45 % N 0.06 % S													
1259-1B	3779	Harshaw	H-Coal	780	2710	3.01	0.268	3630	0.166	-	-	-	17.6	0.105	-	
2		HT-400	Gas Oil	780	2800	2.80	0.249	3910	0.415	-	-	-	17.3	0.098	-	
3		Co-Mo on Al_2O_3	Pdt L428	779	2805	2.79	0.248	4610	0.662	925	1.42	100.0	17.3	0.108	-	
4				810	2800	4.00	0.355	3890	1.009	-	-	-	17.0	0.098		
5				809	2810	4.00	0.355	4200	1.363	-	-	-	17.4	0.088	-	
6				810	2785	4.00	0.355	4340	1.718	945	1.41	98.6	17.2	0.078	-	
7A				780	2775	2.60	0.231	4250	1.834	-	-	-	16.5	0.086	-	8.6
1260-1B	3556	American	H-Coal	777	2010	0.53	0.065	4350	0.046	1707	2.17	93.3	7.3	0.344	14.7	
2		Cyanamid	Fuel Oil	777	2000	0.51	0.062	4563	0.107	-	-	-	1.1	0.482	-	
3		HDS 2A	Pdt L438	779	2010	0.43	0.053	4990	0.168	918	1.17	96.7	-3.2	0.539	31.2	20.6
		Co-Mo on Al_2O_3	-12.6 °API 0.841 % N 0.59 % S 41.6 W % 945°F+													
1261-1B	3556	See Above	H-Coal	808	2810	0.50	0.061	5320	0.047	1914	2.61	93.0	13.3	0.267	12.3	
2			Fuel Oil	805	2820	0.50	0.061	5070	0.111	-	-	-		0.331	-	
3			Pdt L440 3.2 oAPI 0.810 % N 0.37 % S 32.1 W % 955°F+	806	2790	0.50	0.061	4862	0.172	1634	2.22	93.8	9.2	0.372	16.9	19.4

DENITROGENATION OF COAL LIQUIDS FROM SOLVENT REFINED COAL PROCESS

Feed L446 - Blend of 40 W % SRC Product and 60 W % SRC SRC Solvent,
-6.8 °API, 1.07% N, 0.67% S, 34.7 W % 975°F+, 8.5 W % 975°F+ Benzene - Insoluble

Run No.-Period Unit 115	Catalyst HRI No.	Catalyst Manufacture Identification	Temp. °F	Pressure Psig	Space Velocity V/Hr/V	Space Velocity B/D/Lb	Excess H_2 Bbl/Lb	Cat. Age Bbl/Lb	H_2 Consumption SCF/Bbl	H_2 Consumption W %	Liquid Product W % Output Basis	Liquid Product °API	Liquid Product % N	Liquid Product 975°F+ W % Total	Liquid Product 975°F+ W % Insoluble	Spent Catalyst % C
1262-1B	3556	American	845	2825	0.51	0.061	5890	0.082				12.8	0.337			
2		Cyanamid	849	2800	0.64	0.068	5500	0.150				12.0	0.355			
3		HDS 2A	847	2785	0.57	0.068	6030	0.218	2420	3.35	91.5	10.5	0.399	16.8	0.38	30.1
1263-1B	3849	American	850	2835	0.51	0.065	7600	0.067				10.5	0.241			
2		SN4412B	850	2790	0.53	0.067	4830	0.132				3.3	0.533			
3		Co-Mo, 1/16"	854	2795	0.71	0.089	3150	0.256	810	1.12	95.4	2.7	0.653	24.1	5.09	39.1
1264-1B	3850	American	850	2825	0.51	0.065	6170	0.082				12.7	0.248			
2		Cyanamod	849	2805	0.44	0.057	6840	0.144				11.3	0.336			
3		SN4412A	850	2785	0.50	0.064	5490	0.210	2730	3.79	90.3	11.6	0.431	17.2	0.62	31.9
1265-1B	3851	American	850	2790	0.49	0.065	6010	0.077				8.8	0.418			
2		Cyanamid	852	2810	0.42	0.056	5760	0.138				9.1	0.444			
3		Ni-W, 1/16"	847	2810	0.53	0.070	5440	0.210	2270	3.22	90.8	8.7	0.615	11.9	0.66	27.1
1266-1B	3556	American	819	2800	0.54	0.067	3340	0.073				11.0	0.375			
2		Cyanamid	813	2800	0.53	0.066	2830	0.139				9.4	0.571			
3		Ni-W, 1/16"	810	2780	0.51	0.063	4560	0.203	2230	2.95	94.1	8.6	0.529	20.3	0.37	25.3
1267-1B	3850	American	807	2810	0.28	0.062	4940	0.062				14.1	0.249			
2		Cyanamid	811	2830	0.50	0.064	5460	0.126				15.6	0.258			
3		Ni-W, 1/16"	815	2805	0.53	0.068	5250	0.193	2890	3.82	94.0	13.5	0.365	12.3	0.14	21.5
1268-1B/1/	3850	American	776	2810	0.53	0.069	5610	0.073				18.8	0.182			
2		Cyanamid	780	2800	0.53	0.069	4180	0.143				19.9	0.169			
3		Ni-W, 1/16"	781	2780	0.43	0.056	5380	0.191	3220	4.7	97.4	23.7	0.90	-	-	10.7

* Feed HRI 3861 SRC Solvent, 1.8° API, 0.69% N, 0.67% S

DENITROGENATION OF COAL LIQUIDS FROM SOLVENT REFINED COAL PROCESS

Run No.-Period Unit 115	HRI No.	Manufacture Identification	Temp. °F	Pressure Psig	Space Velocity V/Hr/V	Space Velocity B/D/Lb	Excess H_2 Bbl/Lb	Cat. Age Bbl/Lb	H_2 Consumption SCF/Bbl	H_2 Consumption W %	Liquid Product W % Output Basis	Liquid Product °API	Liquid Product % N	Liquid Product 975°F+ W % Total	Liquid Product 975°F+ W % Insoluble	Spent Catalyst % C
1269-1B	3850	American	777	2805	0.45	0.058	6600	0.052				12.8	0.232			
2		Cyanamid	777	2800	0.56	0.023	3710	0.120				10.7	0.268			
3		SN4412A Ni-Co 1/16" Extrudate	780	2790	0.56	0.073	4180	0.191	1900	2.51	96.4	5.8	0.638	21.4	.41	23.1
1270-1B	3866	SN4424	813	2810	0.53	0.067	2880	0.064				10.5	0.256			
2		1/16" Size	811	2800	0.51	0.064	4000	0.128				12.8	0.311			
3			813	2785	0.51	0.064	3680	0.193	2637	3.49	94.3	11.6	0.396	13.5	1.35	22.8
1271-1B	3867	SN4425	810	2800	0.47	0.075	5050	0.069				14.0	0.396			
2		1/16" Size	813	2795	0.51	0.064	7620	0.140				10.6	0.390			
3			810	2770	0.49	0.061	4400	0.204	2663	3.53	94.7	10.7	0.369	14.0	1.41	24.2
1272-1B	3850	American	803	2825	0.39	0.052	6630	0.066				14.1	0.265			
2B		Cyanamid	802	2780	0.33	0.044	6680	0.117				12.0	0.416			
3B		SN4412A	806	2810	0.51	0.067	3550	0.183	2350	3.20	93.3	9.6	0.368	14.0	.10	28.2
4B		Ni-Co 1/16"	813	2815	0.51	0.066	4980	0.248				9.0	0.372			
5B		Extrudate	811	2815	0.49	0.064	3830	0.311				8.0	0.550			
6B			811	2790	0.45	0.059	6990	0.374	2360	3.27	91.6	7.6	0.619	17.9	.31	28.2
7B			805	2800	0.26	0.034	10640	0.422				9.1	0.663			
1273-1B	3849	American	812	2805	0.53	0.068	5840	0.075				7.2	0.599			
2		Cyanamid	810	2795	0.53	0.068	8770	0.144				11.2	0.318			
3		SN4412B Co-Mo, 1/16" Extrudate	803	2815	0.52	0.067	7150	0.211	2640	3.60	92.0	10.2	0.544	14.7	.15	24.2
1274-1B	3851	American	812	2765	0.49	0.067	4170	0.038				10.2	0.587			
2		Cyanamid	810	2790	0.55	0.075	3620	0.111				9.8	0.533			
3		SN4412C Ni-W, 1/16" Extrudate	802	2800	0.52	0.071	3870	0.182	2340	3.16	96.6	7.7	0.695	18.0	.21	15.8
1275-1B	3556	American	809	2000	0.57	0.070	4600	0.078				4.0	0.665			
2		Cyanamid	808	2000	0.53	0.065	4300	0.145				7.6	0.429			
3		HDS-1442A	810	1990	0.50	0.061	5260	0.207	1770	2.42	91.3	7.0	.600	16.9	.48	26.2
1276-1B	3850	American	809	1965	0.57	0.076	5010	0.080				2.5	0.683			
2		Cyanamid	809	1975	0.53	0.070	4670	0.151				8.1	0.494			
3		SN4412A Ni-Co, 1/16" Extrudate	-	1945	0.54	0.062	4610	0.205	2070	3.02	91.2	9.0	0.408	15.9	.37	30.4
1277-1B	3849	American	809	1995	0.51	0.065	5120	0.068				9.3	0.372			
2		Cyanamid	810	2015	0.49	0.062	7280	0.132				9.8	0.390			
3		SN4412B Co-Mo, 1/16" Extrudate	811	1995	0.50	0.064	4860	0.196	2220	2.95	90.6	8.4	0.484	16.8	.25	23.6

DENITROGENATION OF COAL LIQUIDS FROM SOLVENT REFINED COAL PROCESS

Run No.-Period Unit 115	HRI No.	Manufacture Identification	Temp. °F	Pressure Psig	Space Velocity V/Hr/V	Space Velocity B/D/Lb	Excess H_2 Bbl/Lb	Cat. Age Bbl/Lb	H_2 Consumption SCF/Bbl	H_2 Consumption W %	Liquid Product W % Output Basis	Liquid Product °API	Liquid Product % N	Liquid Product 975°F+ W % Total	Liquid Product 975°F+ W % Insoluble	Spent Catalyst % C
1278-1B	3851	American	808	1985	0.48	0.066	5630	0.069				7.7	0.527			
2		Cyanamid	810	2025	0.49	0.067	6360	0.137				7.7	0.632			
3		SN4412B Co-Mo, 1/16" Extrudate	809	1980	0.51	0.071	4710	0.209	1760	2.44	89.5	6.7	0.630	17.6	.31	21.1
1279-1B	3904	American	805*	2790	0.51	0.058	5980	0.064				3.8	0.615			
2		Cyanamid	809	2810	0.53	0.060	5170	0.123				11.7	0.330			
3		ACCO-SN4474	808	2775	0.55	0.063	5630	0.186	2500	3.56	91.8	8.5	0.492	16.1	.56	25.1
1280-1B	3905	American	815*	2795	0.55	0.062	5450	0.063				14.2	0.228			
2		Cyanamid	821	2800	0.53	0.060	4770	0.123				14.4	0.207			
3		ACCO-SN4475	828	2785	0.52	0.059	3630	0.182	2840	3.84	92.4	12.4	0.274	11.5	.10	23.3
1281-1B	3904	See Above	846	2795	0.47	0.055	5910	0.059				15.1	0.275			
2			839	2805	0.51	0.059	5480	0.118				14.2	0.467			
3			851	2800	0.51	0.059	4480	0.178	3040	4.07	90.1	12.8	0.320	10.5	.08	27.4
1282-1B	3905	See Above	847	2650	0.53	0.059	5110	0.059				8.2	0.408			
2			851	2795	0.50	0.056	5000	0.116				12.1	0.438			
3			855	2785	0.51	0.057	4560	0.173	2880	3.97	88.8	11.6	0.331	12.1	.09	28.5
1283-1B	3866	American	843	2815	0.54	0.069	4770	0.069				13.7	0.269			
2		Cyanamid	846	2795	0.55	0.069	4750	0.138				10.7	0.372			
3		SN4424	842	2790	0.53	0.068	5510	0.207	2380	3.26	88.0	4.8	0.711	18.3	2.93	35.7
1284-1B	3867	American	849	2810	0.50	0.063	4680	0.063				12.8	0.299			
2		Cyanamid	851	2790	0.51	0.065	7990	0.125				13.2	0.241			
3		SN4425	852	2790	0.51	0.065	5740	0.192	3080	4.28	87.4	13.0	0.306	9.5	.10	31.0
1285-1B	3905	American	827	2800	0.54	0.062	4120	0.064				16.9	0.218			
2		Cyanamid	825	2805	0.53	0.060	3970	0.124				15.5	0.274			
3		ACCO-SN4475	823	2790	0.51	0.058	3660	0.181	2670	3.43	92.3	14.6	0.319	10.9	.04	24.3
1286-1B	3911	American	820	2800	0.50	0.043	4940	0.045				15.7	0.198			
2		Cyanamid	819	2785	0.50	0.043	5280	0.089				14.8	0.225			
3		SN4510	818	2815	0.47	0.041	5280	0.131	2990	3.89	91.4	13.4	0.227	10.0	.02	22.1
1287-1B	3922	Armak	826	2805	0.42	0.035	6030	0.044				7.0	0.560			
2		PA24268	822	2795	0.47	0.040	4680	0.086				14.6	0.266	11.2	.30	
3			810	2800	0.50	0.042	5490	0.129	3010	3.96	87.9	12.4	0.282			19.1
1288-1B	3928	Armak	805	2800	0.50	0.050	3690	0.052				14.9	0.343			
2		PA24266	811	2790	0.55	0.056	4540	0.106				14.5	0.272			
3			809	2780	0.50	0.051	6060	0.158	2900	3.82	89.7	11.4	0.324	13.5	.42	19.8
1289-1B	3905	See Above	816	2805	0.51	0.058	5530	0.058				16.6	0.151			
2			812	2775	0.52	0.116	4220	0.116				13.9	0.236			
3			811	2790	0.54	0.181	5320	0.181	3190	4.22	91.1	12.6	0.294	14.1	.14	18.8
1290-1B	3298	See Above	816	2820	0.49	0.050	5910	0.049				10.3	0.317			
2			816	2780	0.49	0.050	5440	0.099				8.2	0.366			
3			815	2800	0.49	0.049	6000	0.150	2531	3.34	91.1	8.7	0.398	17.2	.20	23.2
1291-1B	3928	See Above	810	2785	0.54	0.055	3200	0.054				7.5	0.415			
			809	2775	0.53	5740	0.107					13.2	0.271			
			809	2810	0.051	0.052	4980	0.159	3110	4.11	92.7	13.0	0.266	13.0	.19	15.0

DENITROGENATION OF COAL LIQUIDS FROM SOLVENT REFINED COAL PROCESS

Run No.-Period	HRI No.	Manufacture Identification	Temp. °F	Pressure Psig	Space Velocity V/Hr/V	Space Velocity B/D/Lb	Excess H_2 Bbl/Lb	Cat. Age Bbl/Lb	H_2 Consumption SCF/Bbl	H_2 Consumption W %	Liquid Product W % Output Basis	Liquid Product °API	Liquid Product % N	Liquid Product 975°F+ W % Total	Liquid Product 975°F+ W % Insoluble	Spent Catalys % C
Unit 115																
1292-1B	3959	Armak	804	2800	0.54	0.054	4850	0.057				16.8	0.174			
2		PA25137	806	2800	0.53	0.54	6280	0.105				14.2	0.171			
			805	2800	0.51	0.052	4770	0.158	3140	4.15	91.4	12.8	0.284	10.5	.22	17.5
1293-1B	3966	Armak	811	2795	0.49	0.057	6450	0.057				16.1	0.197			
2		PA24738	808	2785	0.49	0.057	5240	0.114				14.2	0.262			
3		Ketjen Ni-Mo	816	2805	0.50	0.059	4730	0.170	3230	4.27	92.1	13.4	0.250	12.5	.13	26.6
4			816	2805	0.52	0.061	4730	0.232				11.9	0.249			
5			812	2795	0.50	0.059	4570	0.291				11.5	0.361			
6			813	2790	0.51	0.060	5820	0.351	2830	3.74	90.0	11.6	0.370	12.0	.42	26.6
7			813	2760	0.49	0.057	5140	0.410				10.9	0.385			
8			813	2800	0.50	0.058	4320	0.467				10.1	0.377			
9			813	2790	0.51	0.059	7200	0.527				9.9	0.408			
10			811	2800	0.50	0.059	5340	0.586				10.3	0.388			
11			816	2815	0.52	0.061	4790	0.646				10.1	0.394			26.6
12			811	2800	0.56	0.065	4330	0.711	2340	3.09	90.4	6.6	0.561	19.6	1.89	
13			809	2795	0.54	0.062	6080	0.774				2.7	0.831			
14			811	2800	0.53	0.061	5200	0.832				2.2	0.764			
15			810	2800	0.53	0.062	4075	0.893	1610	2.13	93.2	3.0	0.766	23.3		26.6
1294-1B	3966	See Above	811	2785	0.51	0.122	4520	0.117				7.9	0.487			
2			803	2795	0.50	0.118	4690	0.235				7.4	0.547			
3			812	2805	0.49	0.117	5800	0.353	2310	3.05	92.6	7.6	0.494	17.5	.20	17.7
4			809	2800	0.50	0.120	5280	0.472				6.9	0.595			
5			804	2780	0.51	0.122	3570	0.593				5.5	0.636			
6			808	2780	0.49	0.115	5250	0.710	1990	2.63	92.9	6.5	0.642	18.2	.55	17.7
7			807	2780	0.54	0.128	7720	0.836				5.5	0.702			
8			808	2805	0.53	0.126	5550	0.960				5.4	0.696			
9			808	2785	0.50	0.118	5720	1.076				5.5	0.680			
10			806	2785	0.55	0.131	5740	1.209				5.3	0.707			
11			808	2775	0.54	0.132	5040	1.338				4.8	0.749			
12			806	2800	0.54	0 128	5930	1.461				5.3	0.656			
13			806	2780	0.53	0.125	4590	1.586				3.9	0.751			
14			808	2820	0.43	0.101	6240	1.701				4.4	0.702			
15			803	2790	0.50	0.118	4660	1.818	1840	2.43	93.7	5.1	0.649	19.4	.74	17.7

APPENDIX B

SUMMARY OF OPERATING CONDITIONS, PRODUCT DISTRIBUTION, HYDROGEN CONSUMPTION, 975^{o}F+ CONVERSION, AND HETEROATOM REMOVAL

The product distribution was normalized to give complete material balance closure by prorating the weights of liquid product and the gas product equal to the weight of feed plus hydrogen consumed.

H_2S, NH_3 and H_2O were calculated from the sulfur, nitrogen and oxygen balances of the feed and the liquid product. Hydrogen consumption was the sum of the increase between the hydrogen contents of the liquid and gas products and that of the feed and the hydrogen required for formation of H_2S, NH_3 and H_2O.

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCES

Run Number	115-1285	115-1286	115-1287	115-1288	115-1289	115-1290	115-1291	115-1292	115-1293	115-1294
Period	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B
Hours on Stream	59-71	59-71	60-72	60-72	60-72	60-72	59-71	59-71	60-72	60-72
Feed (HRI No.)	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446
Catalyst (HRI No.)	3905	3911	3922	3928	3905	3928	3928	3959	3966	3966
Catalyst Age, Bbl/Lb	0.181	0.131	0.129	0.158	0.181	0.150	0.159	0.158	0.143	0.353
OPERATING CONDITIONS										
Pressure, psig, outlet	2790	2815	2800	2785	2790	2800	2810	2800	2800	2800
Reactor Temperature	811	811	810	809	811	806	809	809	813	810
Space Velocity, V_f/Hr/Vcat	0.51	0.47	0.50	0.50	0.54	0.49	0.51	0.51	0.50	0.98
Space Velocity, Bbl/D/Lb	0.058	0.041	0.042	0.051	0.063	0.049	0.052	0.052	0.050	0.117
Hydrogen Rate, SCF/Bbl (Outlet)	3430	3980	5500	6060	4970	4810	4750	4470	4460	5480
YIELDS, W % ON OUTPUT BASIS										
$CO+CO_2$	0.04	0.13	0.86	0.62	0.29	0.06	0.14	0.08	0.12	0.30
$H_2S+NH_3+H_2O$ (Calculated)	6.58	6.35	6.10	6.02	6.58	6.54	6.43	6.65	6.59	5.99
C_1-C_3	3.09	3.93	3.24	3.69	4.03	3.86	3.08	4.12	3.13	2.71
C_4-C_6	1.42	2.04	5.81	3.76	2.17	1.78	1.75	1.90	2.30	1.40
IBP-975°F	82.23	82.29	78.09	77.61	78.29	75.42	80.64	81.79	80.61	76.41
975°F+ (Benzene Soluble)	10.02	9.12								
975°F+ (Benzene Insoluble)	0.04	0.02								
975°F+ (Toluene Soluble)			9.59	11.73	12.72	15.49	11.87	9.35	11.31	16.02
975°F+ (Toluene Insoluble)			0.26	0.38	0.13	0.18	0.18	0.24	0.20	0.19
Ash	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.03
Total	103.43	103.89	103.96	103.82	104.22	103.34	104.11	104.15	104.27	103.05
Hydrogen Consumption, SCF/Bbl	2670	2990	3010	2900	3190	2531	3110	3140	3230	2310
975°F+ Conversion, %	71.01	73.65	71.62	65.09	62.97	54.85	65.27	72.35	66.82	53.29
Benzene Insoluble Conversion, %	99.8	99.9								
Toluene Insoluble Conversion, W %			91.8	91.5	96.2	95.9	96.5	93.0	95.3	94.7
HETEROATOM REMOVAL										
Nitrogen	70.2	78.8	73.6	69.7	72.5	62.8	69.2	73.8	76.6	53.8
Sulfur	99	99	100	100	99.3	98.5	97.8	98.0	95	95
Oxygen	89.6	83.1	79.3	77.9	89.0	90.6	89.6	91.8	90.2	88.3
SPENT CATALYST ANALYSIS										
Carbon, %	24.30	22.07	19.13	19.78	18.78	23.20	14.99	17.53	26.6	17.7
Hydrogen, %	1.44	1.43	1.30	1.32	1.33	1.31	1.18	1.14	1.15	0.90
Sulfur, %	-	-	-	-	6.06	5.42	0.44	0.44	6.01	6.28
Nitrogen, %	.519	.485	5.81	5.37	0.12	0.50	6.11	6.08	0.58	0.46
Titanium								0.305		0.307

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCES

Run Number	115-1273	115-1274	115-1275	115-1276	115-1277	115-1278	115-1279	115-1280	115-1231	115-1282	115-1283	115-1284
Period	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B
Hours on Stream	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72
Feed (HRI No.)	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446
Catalyst (HRI No.)	3849	3851	3556	3850	3849	3851	3904	3905	3904	3905	3866	3867
Catalyst Age, Bbl/Lb	0.0211	0.182	0.207	0.205	0.196	0.209	0.186	0.182	0.178	0.173	0.207	0.192
OPERATING CONDITIONS												
Pressure, psig, outlet	2815	2800	1990	1950	2000	1980	2775	2785	2800	2785	2790	2790
Reactor Temperature	804	800	810	810	811	809	808	808	851	851	848	848
Space Velocity, $V_f/Hr/V_{cat}$	0.52	0.52	0.50	0.54	0.50	0.51	0.55	0.52	0.51	0.51	0.53	0.51
Space Velocity, Bbl/D/Lb	0.067	0.071	0.061	0.062	0.064	0.071	0.063	0.059	0.059	0.057	0.068	0.065
Hydrogen Rate, SCF/Bbl (Outlet)	7150	3870	5250	4600	4850	4700	5340	3360	4090	4120	5040	5240
YIELDS, W % ON OUTPUT BASIS												
$CO+CO_2$	0.31	0.25	0.15	0.40	0.04	0.19	0.43	0.17	0.10	0.27	0.19	0.35
$H_2S+NH_3+H_2O$ (Calculated)	6.43	6.25	6.50	6.66	6.73	6.55	5.98	6.30	6.43	6.46	6.43	6.70
C_1-C_3	3.54	2.95	3.27	3.64	4.08	4.30	3.33	3.35	5.36	5.92	6.35	6.57
C_4-C_6	1.24	1.05	1.15	1.16	1.53	1.85	1.99	1.61	2.07	2.47	2.31	3.20
IBP-975°F	78.52	75.96	75.90	76.66	75.34	73.77	77.03	81.77	80.64	78.09	71.87	79.14
975°F+ (Benzene Soluble)	13.39	16.47	15.00	14.16	14.98	15.47	14.27	10.53	9.39	10.67	13.52	8.22
975°F+ (Benzene Insoluble)	0.14	0.20	0.44	0.34	0.23	0.28	0.51	0.09	0.07	0.08	2.58	0.09
Ash	0.03	0.03	0.01	0.01	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01
Total	103.60	103.16	102.42	103.02	102.95	102.44	103.56	1-3.84	104.07	103.97	103.26	104.28
Hydrogen Consumption, SCF/Bbl	2640	2340	1770	2070	2220	1760	2500	2840	3040	2880	2380	3080
975°F+ Conversion, W %	61.00	51.95	55.51	58.23	56.16	54.59	57.40	69.38	72.74	69.02	53.61	76.06
Benzene Insoluble Conversion, %	99	99	98.2	98.7	99.1	98.9	98.3	99.7	99.4	99.2	73.5	99.2
HETEROATOM REMOVAL, %												
Nitrogen	4.91	35.0	43.9	61.9	54.8	41.1	54.1	74.5	70.1	69.1	33.6	72.1
Sulfur	92.2	99	-	-	-	-	95.8	98.7	799	799	91.2	799
Oxygen	93.0	92.6	-	-	-	-	81.9	83.7	86.5	86.7	95.0	90.8
SPENT CATALYST ANALYSIS, W %												
Carbon	24.17	15.79	26.15	30.37	23.65	21.11	25.13	23.28	27.45	28.53	35.73	31.03
Hydrogen	1.24	1.02	1.10	0.97	1.28	1.36	1.52	1.39	1.65	1.56	1.81	1.65
Sulfur	-	-	-	-	-	-	-	-	-	-	-	-
Nitrogen	-	-	-	-	-	-	0.80	0.61	-	-	-	-

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCES

Run Number	115-1260	115-1261	115-1262	115-1263	115-1264	115-1265	115-1266	115-1267	115-1268	115-1269	115-1270	115-1271	115-1272
Period	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B	3B
Hours on Stream	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72	60-72
Feed (HRI No.)	L-438	L-440	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446	L-446
Catalyst (HRI No.)	3556	3556	3556	3849	3850	3851	3556	3850	3850	3850	3866	3867	3850
Catalyst Age, Bbl/Lb	0.168	0.172	0.218	0.256	0.210	0.210	0.203	0.193	0.191	0.191	0.193	0.204	0.183
OPERATING CONDITIONS													
Pressure, psig, outlet	2010	2790	2785	2795	2785	2810	2785	2805	2780	2790	2785	2770	2810
Reactor Temperature	774	806	850	850	847	850	810	810	781	780	813	810	806
Space Velocity, V_f/Hr/Vcat	0.43	0.50	0.57	0.71	0.50	0.53	0.51	0.53	0.43	0.56	0.51	0.49	0.51
Space Velocity, Bbl/D/Lb	0.53	0.061	0.68	0.089	0.064	0.070	0.063	0.068	0.056	0.073	0.64	0.061	0.067
Hydrogen Rate, SCF/Bbl (Outlet)	4990	4855	6025	3150	5491	5435	4564	5254	5382	4184	3682	4405	3550
YIELDS, W % ON OUTPUT BASIS													
$CO+CO_2$	-	-	3.38	0.83	1.63	2.73	0.21	0.40	0.18	0.07	0.07	0.39	0.14
$H_2S+NH_3+H_2O$ (Calculated)	2.71	3.51	1.32	1.05	1.28	1.24	4.12	3.77	3.93	4.41	4.06	4.03	5.07
C_1-C_3	1.48	2.22	5.34	2.73	6.38	5.88	3.10	3.07	3.22	1.63	3.36	2.27	3.22
C_4-C_6	0.30	2.17	1.81	1.06	4.21	2.54	1.44	2.58	0.00	0.00	1.34	2.05	1.49
IBP-975°F	66.29	77.15	76.12	76.06	74.74	80.01	72.57	82.43	97.37	75.75	81.81	81.44	80.20
975°F+ (Benzene Soluble)	30.06 *	15.69 *	15.02	14.52	14.97	10.21	18.14	11.43	0.00	20.22	11.50	11.92	12.97
975°F+ (Benzene Insoluble)			0.35	4.86	0.56	0.60	0.35	0.13	0.00	0.40	1.27	1.34	0.09
Ash	0.02	1.48	0.01	0.02	0.01	0.01	0.02	0.02	0.00	0.04	0108	0.09	0.01
Total	101.17	102.22	103.35	101.12	103.79	103.22	102.95	103.82	104.70	102.51	103.49	103.53	103.20
Hydrogen Consumption, SCF/Bbl	918	1634	2420	810	2730	2270	2230	2890	3220	1900	2637	2663	2350
975°F+ Conversion, W %	21.8	42.1	55.71	44.17	55.26	68.85	46.73	66.68	0	40.57	63.20	61.79	62.38
Benzene Insoluble Conversion, %	-	-	95.2	27.5	92.5	92.2	96.6	98.4	0	95.41	96	94	99.7
HETEROATOM REMOVAL, %													
Nitrogen	35.9	54.1	62.7	39.0	59.7	42.5	50.6	65.9	92.7	48.6	63.0	65.5	72.9
Sulfur	23.9	792	68.3	74.7	65.0	94.3	83.7	93.3	92.1	86.3	795	795	95
Oxygen	33.3	69.3	89.8	16.8	32.0	64.4	-	-	-	90.3	64.7	63.1	-
SPENT CATALYST ANALYSIS, W %													
Carbon			30.14	39.14	31.93	27.12	25.29	21.47	10.68	23.07	22.73	24.18	28.22
Hydrogen			1.24	1.64	1.32	1.15	1.20	0.91	0.85	1.27	1.30	1.37	1.31
Sulfur			-	-	-	-	-	-	-	-	-	-	-
Nitrogen			0.464	0.649	0.524	0.517	-	-	0.264	0.547	-	-	-

*The value represents total 975°F+